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Supporting Information

Diverse N-Heterocyclic Ring Systems via Aza-Heck Cyclizations of N-(Pentafluorobenzoyloxy)sulfonamides

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Supporting Information

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General Experimental Details

Unless stated, all materials were purchased from commercial sources (Acros, Aldrich, Alfa Aesar, Fluorochem and Strem) and used without any further treatment. Reagents requiring purification were purified using standard laboratory techniques according to methods published by Perrin, Armarego, and Perrin (Pergamon Press, 1966). Catalytic reactions were carried out in Young-type re-sealable tubes. Anhydrous solvents were obtained by distillation using standard procedures or by passage through drying columns supplied by Anhydrous Engineering Ltd. High-boiling solvents were removed from the reaction crude employing rotary evaporators connected with high-vacuum pumps.

Flash column chromatography (FCC) was performed using silica gel (Aldrich 40-63 µm, 230-400 mesh). Thin layer chromatography was performed using aluminium backed 60F254 silica plates. Visualization was achieved by UV fluorescence or a basic KMnO4 solution and heat. Proton nuclear magnetic resonance spectra (NMR) were recorded at 400 MHz or 500 MHz. 13C NMR spectra were recorded at 100 MHz or 125 MHz as stated. Chemical shifts (δ) are given in parts per million (ppm). Peaks are described as singlets (s), doublets (d), triplets (t), quartets (q), multiplets (m) and broad (br.). Coupling constants (J) are quoted to the nearest 0.5 Hz. All assignments of NMR spectra were based on 2D NMR data (COSY, HSQC and HMBC). In situ yields were determined by employing 1,3,5-trimethoxybenzene as internal standard. Mass spectra were recorded using a Bruker Daltonics FT-ICR-MS Apex 4e 7.0T FT-MS (ESI+ mode) and a Shimadzu GCMS QP2010+ (EI+ mode).

Infrared spectra were recorded on a Perkin Elmer Spectrum Two FTIR spectrometer as thin films or solids compressed on a diamond plate. Melting points were determined using Stuart SMP30 melting point apparatus and are reported uncorrected. Enantiomeric excess was determined by integration of chromatogram peaks. Chiral SFC was performed on an Agilent 1260 Infinity SFC Control Module system equipped with a quaternary pump, diode array detector and column thermostat under the conditions specified. The numbering of compound structures does not necessarily reflect the numbering contained in the systematic names.
Experimental Procedures and Data

General procedure A: Mitsunobu reaction employing diisopropyl azodicarboxylate

To a solution of alcohol (1.0 eq.), hydroxylamine-derived pronucleophile (1.3 eq.) and PPh₃ (2.0 eq.) in anhydrous THF:PhMe (2:1, 30 mL/mmol) at 0 °C was added a solution of DIAD (1.5 eq.) in anhydrous PhMe (10 mL/mmol) dropwise. The reaction mixture was stirred at room temperature overnight before being concentrated *in vacuo* and loaded directly onto silica gel for purification by FCC.

General procedure B: Mitsunobu reaction employing diethyl azodicarboxylate

To a solution of alcohol (1.0 eq.), hydroxylamine-derived pronucleophile (1.5 eq.) and PPh₃ (2.0 eq.) in anhydrous PhMe:THF (3:1, 8 mL/mmol) at 0 °C was added a solution of DEAD (2.0 eq.) in anhydrous PhMe (2 mL/mmol) dropwise. The reaction mixture was stirred at room temperature overnight before being concentrated *in vacuo* and loaded directly onto silica gel for purification by FCC.

General procedure C: Alkylation of diethyl malonate

To a suspension of NaH (60% weight in mineral oil, 2.0 eq.) in anhydrous THF (approx. 3 mL/mmol) at 0 °C was added diethyl malonate (2.0 eq.) dropwise, the reaction mixture was stirred at this temperature for 1 hour before dropwise addition of allyl bromide (1.0 eq.). The reaction mixture was warmed to room temperature and monitored by TLC. Upon completion, the reaction mixture was poured into a solution of KOH (12 eq.) in water:MeOH (1:1) and stirred for 30 minutes. The reaction mixture was acidified with 10 M aqueous HCl (20 eq.), concentrated to an aqueous solution and extracted with EtOAc (approx. 3 × 5 mL/mmol).

The crude mixture of malonic acids was dissolved in DMF and heated to reflux for 3 hours before being concentrated *in vacuo* to afford the crude decarboxylated product.

General procedure D: Reduction of carboxylic acids or esters

To a solution of carboxylic acid/ester (1.0 eq.) in anhydrous THF or Et₂O (approx. 5 mL/mmol) at 0 °C was added LiAlH₄ (*equivalents specified*) dropwise. The reaction mixture was warmed to room temperature and monitored by TLC. Upon completion, the reaction mixture was cooled to 0 °C before addition of water (1 mL/g of LiAlH₄), 15 % aq. NaOH (1 mL/g of LiAlH₄) and a final portion of water (3 mL/g of LiAlH₄), the resulting mixture was filtered through celite® and washed with DCM. The phases were separated and the aqueous phase extracted with DCM (approx. 2 × 5 mL/mmol), the organic phases were dried over Na₂SO₄ and concentrated *in vacuo* to afford the product.
**General procedure E: Bromination of allylic alcohols**

To a solution of alcohol (1.0 eq.) in Et₂O (approx. 5 mL/mmol) at 0 °C was added PBr₃ (0.50 eq.), the reaction mixture was warmed to room temperature and monitored by TLC. Upon completion the reaction mixture was poured into an aqueous solution of K₂CO₃ (1.0 eq.), the phases were separated and the aqueous phase was extracted with Et₂O (approx. 2 × 4 mL/mmol). The Et₂O phases were dried over Na₂SO₄ and concentrated *in vacuo* afford the product.

**General procedure F: Johnson-Claisen rearrangement**

A solution of propionic acid (0.20 eq.) in triethyl orthoacetate (10 eq.) was heated to 110 °C for 1 hour, after this time allylic alcohol (1.0 eq.) was added and the reaction mixture heated to reflux overnight. Upon cooling to room temperature the reaction mixture was concentrated *in vacuo* to afford the crude product which was purified by FCC.

**General procedure G: Palladium-catalyzed cyclization**

A flame-dried re-sealable tube, fitted with a rubber septum, was charged with cyclization substrate, Pd₂(dba)₃ and P(3,5-(CF₃)₂C₆H₃)₃. The tube was purged with nitrogen, anhydrous solvent and Et₃N were added *via* syringe. The tube was sealed and heated at the specified temperature for the time noted. The reaction mixture was concentrated *in vacuo* and the crude mixture was purified by FCC to afford the pure product.

**Hydroxylamine reagents:**

*N*-Tosyl hydroxylamine

**TsNHOH**

This compound was prepared according to a literature procedure.¹

*The spectroscopic properties were consistent with the data available in the literature.*²

*N*-Tosyl-*O*-pentafluorobenzoyl hydroxylamine (4a)

**TsNHO⁵Bz**

To a suspension of *N*-tosylhydroxylamine (1.00 g, 5.34 mmol) and pentafluorobenzoic acid (1.13 g, 5.34 mmol) in DCM (50 mL) at 0 °C was added a solution of *N*-*N'*-dicyclohexylcarbodiimide (1.21 g, 5.88 mmol) in DCM (50 mL) dropwise. The resulting mixture was stirred at 0 °C overnight before
filtration to remove the white precipitate. The filtrate was concentrated in vacuo and the crude mixture was purified by FCC (gradient elution 2:1 – 1:1 hexane:EtOAc) to afford 4a (1.46 g, yield 72%) as a colorless crystalline solid.

m.p. 102-104 °C (DCM:hexane, needles)

$\nu_{\text{max}}$ / cm$^{-1}$: (solid) 3189 (br s), 1781 (s), 1653 (s), 1597 (m), 1500 (s), 1163 (s).

$\delta$H (400 MHz, CDCl$_3$) 9.01 (1H, s, NH), 7.85 (2H, d, $J = 8.5$ Hz, Ts ArCH), 7.36 (2H, d, $J = 8.5$ Hz, Ts ArCH), 2.45 (3H, s, Ts CH$_3$).

$\delta$C (101 MHz, CDCl$_3$) 158.0 ($^1$Bz $\equiv$O), 146.4 (Ts ArC), 132. (Ts ArC), 130.2 (Ts ArCH), 129.1 (Ts ArCH), 21.9 (Ts CH$_3$).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta$F (377 MHz, CDCl$_3$) -134.7 – -134.8 (2F, m), -144.1 (1F, tt, $J = 21.0$, 6.5 Hz), -158.7 – -158.8 (2F, m).

HRMS: (ESI$^+$) Calculated for C$_{14}$H$_8$F$_5$NNaO$_4$: 403.9986. Found [M+ Na]$^+$: 403.9992.

**N-Tosyl-O-tert-butyldimethylsilyl hydroxylamine**

**TsNHOTBS**

To a suspension of N-tosylhydroxylamine (5.00 g, 26.7 mmol) in anhydrous DCM (approx. 200 mL) at 0 °C was added TBSCl (6.03 g, 40.0 mmol) followed by Et$_3$N (5.58 mL, 40.0 mmol). The reaction mixture was stirred at room temperature before addition of water (200 mL). The phases were separated and the aqueous phase extracted with DCM (2 x 150 mL). The combined organic phases were washed with brine (200 mL), dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude mixture was purified by FCC (eluent 3:1 hexane:EtOAc) to afford the title compound (7.16 g, 89 %) as a crystalline colorless solid.

The spectroscopic properties were consistent with the data available in the literature.³
**N-Mesyl hydroxylamine**

**MsNHOH**

This compound was prepared according to a literature procedure.¹

$\nu_{\text{max}}$ / cm⁻¹: (solid) 3373 (br s), 3253 (s), 3036 (m), 1302 (s), 1154 (s).

$\delta$H (400 MHz, CD$_2$CN) 7.45 (2H, m, NH and OH), 2.95 (3H, s, CH$_3$).

$\delta$C (101 MHz, CD$_2$CN) 36.0 (CH$_3$).


**N-Mesyl-O-pentafluorobenzoyl hydroxylamine (4b)**

**MsNHO$_2$Bz**

To a suspension of N-mesylhydroxylamine (3.48 g, 31.3 mmol) and pentafluorobenzoic acid (6.64 g, 31.3 mmol) in DCM (150 mL) at 0 °C was added a solution of N-N’-dicyclohexylcarbodiimide (7.00 g, 34.5 mmol) in DCM (150 mL) dropwise. The resulting mixture was stirred at 0 °C overnight before filtration to remove the white precipitate. The filtrate was concentrated in vacuo and the crude mixture was purified by FCC (gradient elution 2:1 – 1:1 hexane:EtOAc) to afford 4b (7.20 g, 83%) as a colorless solid.

$\nu_{\text{max}}$ / cm⁻¹: (solid) 3151 (s), 2940 (m), 1759 (s), 1653 (m), 1500 (s), 1324 (s), 1165 (s).

$\delta$H (400 MHz, CDCl$_3$) 8.72 (1H, br s, NH), 3.20 (3H, d, $J = 1.0$ Hz, Ms CH$_3$).

$\delta$C (101 MHz, CDCl$_3$) 39.3 (Ms CH$_3$).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta$F (377 MHz, CDCl$_3$) -134.5 – -134.6 (2F, m), -143.5 (1F, tt, $J = 21.0, 6.5$ Hz), -158.4 – -158.6 (2F, m).

**Substrate synthesis:**

*N*-Pent-4-en-1-yl-*N*-(pentafluorobenzoyloxy)-4-toluenesulfonamide (7a)

![Chemical structure](image)

**General procedure A:** 4-Penten-1-ol (48 μL, 0.475 mmol) and 4a were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7a (139 mg, 70 %) as a crystalline colorless solid. m.p. 89-90 °C (Et₂O:hexane)

ν \text{max} / \text{cm}⁻¹: (solid) 2981 (m), 2927 (m), 1787 (s), 1654 (m), 1595 (m), 1505 (s), 1367 (s), 1170 (s), 1076 (s).

δ \text{H} (400 MHz, CDCl₃) 7.80 (2H, d, \(J = 8.0 \text{ Hz}, \text{ArC}_\text{H}\)), 7.38 (2H, d, \(J = 8.0 \text{ Hz}, \text{ArC}_\text{H}\)), 5.75 (1H, ddt, \(J = 17.0, 10.0, 7.0 \text{ Hz}\), \(\text{C}4\text{-H})\), 5.07 - 4.97 (2H, m, \(\text{C}5\text{-H})\)), 3.23 (2H, br s, \(\text{C}1\text{-H})\)), 2.47 (3H, s, \(\text{Ts C}_3\text{H})\)), 2.20 (2H, dt, \(J = 7.0, 7.0 \text{ Hz}\), \(\text{C}3\text{-H})\)), 1.67 (tt, \(J = 7.0, 7.0 \text{ Hz}\), \(\text{C}2\text{-H})\)).

δ \text{C} (126 MHz, CDCl₃) 156.5 (\(^{11}\text{Bz C}=\text{O}\)), 146.0 (\(\text{ArC}\)), 137.0 (\(\text{C}4\)), 130.2 (\(\text{ArC}\)), 130.0 (\(\text{ArCH}\)), 129.8 (\(\text{ArCH}\)), 116.1 (\(\text{C}5\)), 52.1 (\(\text{C}1\)) , 30.5 (\(\text{C}3\)), 25.9 (\(\text{C}2\)), 21.9 (\(\text{Ts C}_3\)).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

δ \text{F} (377 MHz, CDCl₃) -136.0 (2F, dt, \(J = 19.5, 5.5 \text{ Hz}\)), -146.0 (1F, tt, \(J = 21.0, 5.5 \text{ Hz}\)), -158.9 - -159.1 (2F, m).


**2-(Cyclohex-2-en-1-yl)acetic acid**

![Chemical structure](image)

**General procedure C:** 3-Bromocyclohexene (6.90 mL, 60.0 mmol) was employed to afford the title compound as an orange oil (6.23 g, 74 %) which was used without further purification.

*The spectroscopic properties were consistent with the data available in the literature.*
2-(Cyclohex-2-en-1-yl)ethan-1-ol

\[
\begin{align*}
\text{OH} \\
\end{align*}
\]

**General procedure D:** The preceding carboxylic acid (6.20 g, 44.0 mmol) was employed using anhydrous THF as solvent and 1.7 eq. LiAlH₄ (1M in THF). The crude product was filtered through a short plug of silica to afford the title compound (4.85 g, 87 %) as a yellow oil.

δ_H (400 MHz, CDCl₃) 5.67 (1H, dtd, J = 9.5, 3.5, 2.5 Hz), 5.56 (1H, ddt, J = 9.5, 2.0, 2.0 Hz), 3.71 (2H, tt, J = 7.0, 3.5 Hz), 2.22 (1H, ddt, J = 11.5, 5.5, 2.5, 2.5 Hz), 1.96 (2H, tdd, J = 8.0, 4.0, 2.5 Hz), 1.79 (1H, dtd, J = 12.0, 6.0, 5.5, 2.5 Hz), 1.71 (1H, dqq, J = 12.0, 5.0, 2.5 Hz), 1.61 (1H, dt, J = 13.5, 6.5 Hz), 1.56 – 1.50 (1H, m), 1.49 (1H, s), 1.24 (1H, dddd, J = 12.5, 11.0, 8.5, 2.5 Hz).

δ_C (101 MHz, CDCl₃) 131.6, 127.4, 60.9, 39.2, 31.9, 29.1, 25.3, 21.4.

HRMS: (ESI⁺) Calculated for C₈H₁₄NaO: 149.0937. Found [M+Na⁺]: 149.0932.

*The spectroscopic properties were consistent with the data available in the literature.*

N-2-(Cyclohex-2-en-1-yl)ethan-1-yl-N-(pentafluorobenzoyloxy)-4-toluenesulfonamide (7ba)

\[
\begin{align*}
\end{align*}
\]

**General procedure B:** The preceding alcohol (60.0 mg, 0.475 mmol) and 4a were employed, FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7ba (203 mg, 88 %) as a crystalline colorless solid.

m.p. 81-82 °C (Et₂O:hexane)

ν_max / cm⁻¹: (solid) 2988 (m), 2929 (m), 1790 (s), 1654 (m), 1596 (m), 1503 (s), 1370 (s), 1170 (s).

δ_H NMR (400 MHz, CDCl₃) 7.78 (2H, d, J = 8.0 Hz, Ts ArCH), 7.38 (2H, d, J = 8.0 Hz, Ts ArCH), 5.67 (1H, dtd, J = 10.0, 3.5, 2.5 Hz, C₅-H), 5.46 (1H, ddt, J = 10.0, 2.5, 2.5 Hz, C₄-H), 3.26 (2H, br s, C₁-H₂), 2.46 (3H, s, Ts CH₃), 2.29 (1H, m, C₃-H), 1.94 (2H, dddd, J = 7.0, 5.0, 3.5, 2.5 Hz, C₆-H₂), 1.83 – 1.73 (1H, m, C₈-H), 1.72 – 1.44 (4H, m, C₂-H₂ and C₇-H₂), 1.29 – 1.13 (1H, m, C₈-H').
\( \delta_C \) (101 MHz, CDCl\(_3\)) 156.4 (\( ^6 \text{Bz} C=O \)), 145.9 (Ts ArC), 130.3 (C4), 129.9 x 2 (Ts ArC + Ts ArCH), 129.5 (Ts ArCH), 127.9 (C5), 50.6 (C1), 32.8 (C2 or C7), 32.2 (C3), 28.5 (C8), 25.1 (C6), 21.7 (Ts CH\(_3\)), 21.1 (C2 or C7).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

\( \delta_F \) (377 MHz, CDCl\(_3\)) -136.0 – -136.2 (2F, m), -146.2 (1F, tt, \( J = 21.0, 5.5 \) Hz), -159.0 – -159.2 (2F, m).

HRMS: (ESI\(^+\)) Calculated for C\(_{22}\)H\(_{20}\)F\(_5\)NNaO\(_4\): 512.0925. Found [M+Na]\(^+\): 512.0902.

ORTEP view of 7ba

2-(Cyclohex-2-en-1-yl)ethan-1-yl tosylate

To a solution of 2-(cyclohex-2-en-1-yl)ethan-1-ol (3.95 g, 31.3 mmol) and Et\(_3\)N (7.00 mL, 50.2 mmol) in anhydrous DCM (approx. 100 mL) at 0 °C was added TsCl (9.24 g, 48.5 mmol) in two portions. The reaction mixture was stirred at room temperature for 22 hours before addition of saturated aqueous NaHCO\(_3\) (100 mL), the phases were separated and the aqueous phase was extracted
with DCM (2 x 50 mL). The DCM extracts were dried over Na₂SO₄ and concentrated in vacuo. The crude mixture was purified by FCC (elucent 9:1 petroleum ether 40/60:EtoAc) to afford the title compound (8.43 g, 96 %) as a colorless oil.

νmax / cm⁻¹: (film) 3017 (m), 2927 (m), 2860 (m), 1598 (m), 1448 (m), 1361 (s), 1176 (s).

δH (500 MHz, CDCl₃) 7.80 (2H, d, J = 8.5 Hz, ArCH), 7.35 (2H, d, J = 8.5 Hz, ArCH), 5.66 (1H, ddt, J = 10.0, 4.0, 3.5 Hz, C5-H), 5.42 (1H, ddt, J = 10.0, 2.5, 2.5 Hz, C4-H), 4.10 (2H, t, J = 6.5 Hz, C1-H), 2.45 (3H, s, Ts CH₃), 2.17 (1H, m, C3-H), 1.94 (2H, ddd, J = 5.5, 5.5, 4.0, 2.5 Hz, C6-H₂), 1.74 – 1.54 (4H, m, C2-H, C2-H', C7-H and C8-H), 1.52 – 1.42 (1H, m, C7-H''), 1.18 – 1.11 (1H, m, C8-H').

δC (101 MHz, CDCl₃) 144.7 (ArC), 133.12 (ArC), 130.09 (C4), 129.79 (ArCH), 127.99 (C5), 127.86 (ArCH), 68.64 (C1), 35.01 (C2), 31.35 (C3), 28.45 (C8), 25.08 (C6), 21.61 (Ts CH₃), 21.02 (C7).


N-(2-(Cyclohex-2-en-1-yl)ethyl)-N-((tert-butyl(dimethyl)silyl)oxy)-4-toluenesulfonamide

To a solution of the preceding tosylate (1.82 g, 6.49 mmol) and TsNHOTBS (2.35 g, 7.79 mmol) in DMF (40 mL) was added Cs₂CO₃ (3.81 g, 11.7 mmol). The reaction mixture was stirred for 17 hours before addition of saturated aqueous NH₄Cl (50 mL) and water (50 mL). The reaction mixture was extracted with EtOAc (3 x 80 mL) and the combined organic phases were dried over Na₂SO₄ and concentrated in vacuo. The crude mixture was purified by FCC (gradient elution 29:1 – 19:1 hexane:EtOAc) to afford the title compound (1.95 g, 73 %) as a colorless oil that solidified upon standing.

νmax / cm⁻¹: (solid) 3021 (m), 2928 (s), 2858 (m), 1597 (m), 1461 (m), 1351 (s), 1249 (s), 1164 (s).

δH (500 MHz, CDCl₃) 7.73 (2H, d, J = 8.5 Hz, ArCH), 7.34 (2H, d, J = 8.5 Hz, ArCH), 5.67 (1H, ddt, J = 10.0, 3.5, 3.5 Hz, C5-H), 5.47 (1H, ddt, J = 10.0, 2.0, 2.0 Hz, C4-H), 3.04 – 2.89 (2H, m, C1-H), 2.45 (3H, s, Ts CH₃), 2.08 (1H, dddt, J = 8.5, 6.0, 3.0 Hz, C3-H), 1.95 (2H, tdd, J = 6.0, 3.0, 1.5 Hz, C6-H), 1.78 – 1.71 (1H, m, C8-H), 1.71 – 1.58 (2H, m, C2-H and C7-H), 1.54 – 1.44 (m, 2H C2-H').
and C7-H'), 1.16 (1H, dddd, J = 12.5, 11.0, 8.5, 2.5 Hz, C8-H'), 0.92 (9H, s, Si(CH3)3), 0.30 (3H, s, SiC(CH3)3), 0.29 (3H, s, SiC’H3).

δc (101 MHz, CDCl3) 144.4 (ArC), 130.8 (C4), 130.0 (ArC), 129.9 (ArCH), 129.2 (ArCH), 127.7 (C5), 53.9 (C1), 33.3 (C2), 32.9 (C3), 28.7 (C8), 26.0 (Si(CH3)3), 25.2 (C6), 21.6 (Ts CH3), 21.2 (C7), 18.3 (SiC(CH3)3), -4.2 (2 signals, SiCH3 + SiC’H3).


N-(2-(Cyclohex-2-en-1-yl)ethyl)-N-hydroxy-4-toluenesulfonamide

To a solution of the preceding N-alkyl-N-sulfonyl-O-TBS hydroxylamine (1.45 g, 3.54 mmol) in anhydrous THF (30 mL) was added HF-pyridine (70% weight HF, 7.30 mL). The reaction mixture was stirred at room temperature overnight before being quenched with a solution of K2CO3 (20.0 g) in water (100 mL). The resulting phases were separated the aqueous phase extracted with DCM (3 × 100 mL). The combined organic phases were washed with 1 M aqueous HCl, dried over Na2SO4, filtered through a short plug of silica and concentrated in vacuo to afford the title compound as a colorless crystalline solid (1.01 g, 98 %) which was used in the next step without further purification.

νmax / cm⁻¹: (solid) 3356 (br s), 2921 (m), 2917 (m), 1597 (m), 1437 (m), 1330 (s), 1163 (s), 1088 (s).

δH (500 MHz, CDCl3) 7.80 (2H, d, J = 8.5 Hz, ArCH), 7.39 (2H, d, J = 8.5 Hz, ArCH), 6.28 (1H, s, OH), 5.73 – 5.67 (1H, m, C5-H), 5.57 – 5.52 (1H, m, C4-H), 3.07 – 2.93 (2H, m, C1-H2), 2.48 (3H, s, Ts CH3), 2.21 (1H, dddd, J = 11.5, 5.5, 5.5, 2.5 Hz, C3-H), 1.98 (2H, dddd, J = 6.5, 4.5, 3.0, 1.5 Hz, C6-H2), 1.86 – 1.78 (1H, m, C8-H), 1.73 – 1.64 (2H, m, C2-H and C7-H), 1.59 – 1.46 (2H, m, C2-H’ and C7-H’), 1.22 (1H, dddd, J = 12.5, 11.5, 8.5, 3.0 Hz, C8-H’).

δc (126 MHz, CDCl3) 144.9 (ArC), 130.9 (C4), 129.7 (ArCH), 129.6 (ArCH), 129.4 (ArC), 127.7 (C5), 50.3 (C1), 33.0 (C2), 32.5 (C3), 28.7 (C8), 25.2 (C6), 21.7 (Ts CH3), 21.2 (C7).

**N-2-(Cyclohex-2-en-1-yl)ethyl-N-(methanesulfonyloxy)-4-toluenesulfonamide (7bb)**

To a solution of N-2-(cyclohex-2-en-1-yl)ethyl-N-hydroxy-4-toluenesulfonamide (630 mg, 2.13 mmol) in anhydrous DCM (30 mL) at 0°C was added MsCl (325 μL, 4.19 mmol) followed by Et₃N (590 μL, 4.2 mmol). The reaction mixture was warmed to room temperature and stirred overnight before addition of MeOH (15 mL), saturated aqueous NaHCO₃ (30 mL) and brine (30 mL). The resulting phases were separated and the aqueous phase was extracted with DCM (3 × 30 mL). The organic phases were dried over Na₂SO₄ and concentrated in vacuo.

The crude mixture was purified by FCC (eluent 49:1 toluene:EtOAc) to afford 7bb (660 mg, 83%) as a crystalline colorless solid.

m.p. 101-102 °C (Et₂O:hexane)

ν max / cm⁻¹: (solid) 2921 (m), 2861 (m), 1598 (m), 1451 (m), 1373 (s), 1355 (s), 1175 (s), 1088 (s).

δH (400 MHz, CDCl₃) 7.78 (2H, d, J = 8.0 Hz, ArCH), 7.41 (2H, d, J = 8.0 Hz, ArCH), 5.68 (1H, ddt, J = 10.0, 3.5, 3.0 Hz, C₅-H), 5.51-5.46 (1H, m, C₄-H), 3.37 (3H, s, Ms CH₃), 3.23 (2H, br s, C₁-H₂), 2.49 (3H, s, Ts CH₃), 2.21 – 2.13 (1H, m, C₃-H), 1.94 (2H, ddd, J = 5.5, 5.5, 3.0 Hz, C₆-H₂), 1.82 – 1.61 (4H, m, C₂-H, C₂-H’, C₇-H and C₈-H), 1.57 – 1.44 (1H, m, C₇-H’), 1.28 – 1.13 (1H, m, C₈-H’).

δC (126 MHz, CDCl₃) 146.4 (ArC), 130.6 (C₄), 130.2 (ArCH), 129.9 (ArCH), 129.3 (ArC), 128.0 (C₅), 54.4 (C1), 37.9 (Ms CH₃), 33.2 (C₂), 32.7 (C₃), 28.7 (C₈), 25.3 (C₆), 21.9 (Ts CH₃), 21.3 (C7).

HRMS: (ESI⁺) Calculated for C₁₆H₂₃NNaO₅S₂: 396.0910. Found [M+Na⁺]: 396.0924.

**N-2-(Cyclohex-2-en-1-yl)ethyl-N-(trifluoroacyloxy)-4-toluenesulfonamide (7bc)**

N-2-(Cyclohex-2-en-1-yl)ethyl-N-hydroxy-4-toluenesulfonamide (200 mg, 0.677 mmol) was dissolved in trifluoroacetic anhydride (1.00 mL) and stirred for one hour before being concentrated in
vacuo and analyzed by NMR. These steps were repeated until complete conversion was achieved. **7bc** (263 mg, 0.672 mmol, 99 %) was isolated as an amorphous orange solid. This product was employed in the catalytic reactions immediately due to its instability to hydrolysis.

\[ \nu_{\text{max}} / \text{cm}^{-1} : \text{(solid) 3024 (m), 2926 (m), 1597 (m), 1371 (s), 1220 (s), 1165 (s), 1109 (s)}. \]

δ\( H \) (400 MHz, CDCl\(_3\)) 7.77 (2H, d, \( J = 8.5 \) Hz, ArC\( H \)), 7.42 (2H, d, \( J = 8.5 \) Hz, ArC\( H \)), 5.70 (1H, ddt, \( J = 10.0, 3.5, 3.0 \) Hz, C5-H), 5.46 (1H, ddt, \( J = 10.0, 2.5, 2.5 \) Hz, C4-H), 3.23 (2H, br s, C1-H), 2.49 (3H, s, Ts C\( H_3 \)), 2.30 – 2.19 (1H, m, C3-H), 1.96 (2H, m, C6-H), 1.81 – 1.73 (1H, m, C8-H), 1.72 – 1.64 (1H, m, C7-H), 1.60 – 1.41 (3H, m, C2-H, C2-H\(^\prime\) and C7-H\(^\prime\)), 1.18 (1H, dddd, \( J = 13.0, 10.5, 8.0, 2.5 \) Hz, C8-H\(^\prime\)).

δ\( C \) (101 MHz, CDCl\(_3\)) 146.3 (ArC), 130.1 (ArCH), 130.0 (C4), 129.6 (ArCH), 129.0 (ArC), 128.2 (C5), 50.8 (C1), 32.7 (C2), 32.2 (C3), 28.5 (C8), 25.1 (C6), 21.8 (Ts C\( H_3 \)), 21.0 (C7).

The signal corresponding to the trifluoroacetyl group could not be resolved due to its weak intensity.

δ\( F \) (377 MHz, C\(_6\)D\(_6\)) -73.2 (3F, s).

HRMS: (ESI\(^+\)) Calculated for C\(_{17}\)H\(_{20}\)F\(_3\)NNaO\(_4\): 414.0957. Found [M+Na]\(^+\): 414.0965.

**2-(Cyclopent-2-en-1-yl)ethan-1-ol**

\[ \text{2-(Cyclopent-2-en-1-yl)ethan-1-ol} \]

**General procedure D:** 2-Cyclopentene-1-acetic acid (806 mg, 6.81 mmol) was employed, using anhydrous Et\(_2\)O as the solvent and 2.0 eq. LiAlH\(_4\) (1M in Et\(_2\)O). The title compound (713 mg, 93 %) was isolated as a pale yellow oil.

\[ \nu_{\text{max}} / \text{cm}^{-1} : \text{(film) 3327 (br s), 3051 (m), 2928 (s), 2851 (s), 1614 (m), 1057 (s)}. \]

δ\( H \) (400 MHz, CDCl\(_3\)) 5.74 (1H, ddt, \( J = 6.0, 2.0, 2.0 \) Hz), 5.69 (1H, ddt, \( J = 6.0, 2.0, 2.0 \) Hz), 3.76 – 3.64 (2H, m), 2.82 – 2.72 (1H, m), 2.41 – 2.22 (2H, m), 2.12 – 2.02 (1H, m, 1H), 1.70 (1H, ddt, \( J = 13.5, 6.5, 6.5 \) Hz), 1.62 – 1.52 (1H, m), 1.49 – 1.36 (2H, m).

δ\( C \) (101 MHz, CDCl\(_3\)) 134.6, 130.7, 61.8, 42.1, 38.9, 31.9, 29.8.

*The spectroscopic properties were consistent with the data available in the literature.*
**General procedure B:** The preceding alcohol (53.3 mg, 0.475 mmol) and 4a were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7c (200 mg, 89 %) as a crystalline colorless solid.

m.p. 95-96 °C (Et₂O:hexane, needles)

$\nu_{\text{max}} / \text{cm}^{-1}$: (solid) 3056 (m), 2936 (m), 1792 (s), 1655 (m), 1595 (m), 1504 (s), 1667 (s).

$\delta_H$ (400 MHz, CDCl₃) 7.80 (2H, d, $J = 8.5$ Hz, ArCH), 7.38 (2H, d, $J = 8.5$ Hz, ArCH), 5.74 (1H, ddt, $J = 5.5$, 2.0, 2.0 Hz, C5-H), 5.61 (1H, ddt, $J = 5.5$, 2.0, 2.0 Hz, C4-H), 3.26 (2H, br s, C1-H₂), 2.88 – 2.76 (1H, m, C3-H), 2.47 (3H, s, Ts CH₃), 2.39 – 2.21 (2H, m, C6-H₂), 2.06 (1H, dtt, $J = 13.0$, 8.5, 5.0 Hz, C7-H), 1.70 (1H, dtt, $J = 13.5$, 7.0, 7.0 Hz, C2-H), 1.63 – 1.55 (1H, m, C2-H'), 1.37 (1H, dtt, $J = 13.0$, 9.0, 6.5 Hz, C7-H').

$\delta_C$ (101 MHz, CDCl₃) 146.0 (ArC), 133.7 (C4), 131.6 (C5), 130.2 (ArC), 130.0 (ArCH), 129.8 (ArCH), 51.5 (C1), 42.7 (C3), 32.8 (C2), 32.0 (C6), 29.7 (C7), 21.9 (Ts CH₃).

*The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.*

$\delta_F$ (377 MHz, CDCl₃) -136.0 – -136.1 (2F, m), -146.1 (1F, tt, $J = 21.0$, 5.0 Hz), -159.0 – -159.2 (2F, m).


**(E)-N-Hex-4-en-1-yl-N-(pentafluorobenzoyloxy)-4-toluenesulfonamide (7d)**
General procedure A: The preceding alcohol (58 μL, 0.475 mmol) and 4a were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7d (156 mg, 71 %, 11:1 mixture of E and Z isomers) as a crystalline colorless solid.

ν\text{max} / cm\textsuperscript{-1}: (solid) 2936 (m), 1787 (s), 1652 (m), 1597 (m), 1504 (s), 1368 (s), 1325 (s), 1170 (s).

HRMS: (ESI\textsuperscript{+}) Calculated for C\textsubscript{20}H\textsubscript{18}F\textsubscript{5}NNaO\textsubscript{4}S: 486.0769. Found [M+Na]\textsuperscript{+}: 486.0760.

Spectroscopic data for the major E isomer:

δ\textsubscript{H} (500 MHz, CDCl\textsubscript{3}) 7.79 (2H, d, J = 8.5 Hz, ArCH), 7.37 (2H, d, J = 8.5 Hz, ArCH), 5.44 (1H, dqt, J = 15.0, 6.0, 1.5 Hz, C\textsubscript{5}-H), 5.34 (1H, dtq, J = 15.0, 7.0, 1.5 Hz, C\textsubscript{4}-H), 3.21 (2H, br s, C\textsubscript{1}-H), 2.46 (3H, s, Ts CH\textsubscript{3}), 2.11 (2H, dt, J = 7.0, 7.0, 1.5 Hz, C\textsubscript{3}-H), 1.65 – 1.59 (5H, m, C\textsubscript{2}-H and C\textsubscript{6}-H).

δ\textsubscript{C} (126 MHz, CDCl\textsubscript{3}) 156.3 (\textsuperscript{10}Bz C=O), 145.8 (ArC), 130.1 (ArC), 129.8 (ArCH), 129.6 (ArCH), 129.3 (C4), 126.5 (C5), 52.0 (C1), 29.2 (C3), 26.4 (C2), 21.7 (Ts CH\textsubscript{3}), 17.9 (C6).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

δ\textsubscript{F} (377 MHz, CDCl\textsubscript{3}) -135.9 – -136.0 (2F, m), -146.1 (1F, tt, J = 21.0, 5.5 Hz), -158.9 – -159.1 (2F, m).

Characteristic signals for the minor Z isomer (obtained from 1D TOCSY, irradiated signal at 2.19 ppm):

δ\textsubscript{H} (500 MHz, CDCl\textsubscript{3}) 5.53 – 5.46 (m), 5.35 – 5.25 (m), 3.20 (s), 2.19 (dt, J = 7.5, 7.5 Hz), 1.66 – 1.58 (m).

(E)-6-Phenylhex-4-en-1-ol

\[
\text{Ph} \quad \text{H} \quad \text{OH}
\]

To a solution of Hoveyda-Grubbs 2\textsuperscript{nd} generation catalyst (109 mg, 0.174 mmol) in anhydrous, degassed DCM (80 mL) was added simultaneously 4-penten-1-ol (1.20 mL, 11.6 mmol) and allyl benzene (5.80 mL, 44.0 mmol). The reaction mixture was stirred for 2 days at room temperature before being concentrated in vacuo and purified by FCC (elucent 4:1 toluene:EtOAc) to afford the title compound (0.840 g, 41 %, 7:1 mixture of E and Z isomers) as a brown oil (the coloration was due to the presence of trace amounts of Ru-impurities).
$\nu_{\text{max}} / \text{cm}^{-1}$: (film) 3334 (s), 3026 (m), 2932 (m), 1603 (m), 1494 (s), 1452 (s), 1054 (s).

**Spectroscopic data for the major E isomer:**

$\delta_H$ (400 MHz, CDCl$_3$) 7.36 – 7.28 (2H, m), 7.25 – 7.18 (3H, m), 5.65 (1H, dt, $J = 15.0$, 6.5 Hz), 5.55 (1H, dt, $J = 15.0$, 6.5 Hz), 3.66 (2H, t, $J = 6.5$ Hz), 3.37 (2H, d, $J = 6.5$ Hz), 2.15 (2H, dt, $J = 7.5$, 6.5 Hz), 1.96 (1H, br s), 1.71 – 1.63 (2H, m).

$\delta_C$ (101 MHz, CDCl$_3$) 140.9, 131.1, 129.6, 128.5, 128.4, 125.6, 62.4, 39.1, 32.4, 28.8.

**Characteristic signals for the minor Z isomer:**

$\delta_H$ (400 MHz, CDCl$_3$) 3.45 (2H, d, $J = 7.0$ Hz), 2.28 (1H, dt, $J = 7.0$, 7.0 Hz).

*The spectroscopic properties were consistent with the data available in the literature.*

**(E)-N-6-Phenylhex-4-en-1-yl-N-(pentafluorobenzoyloxy)-4-toluenesulfonamide (7e)**

**General procedure B:** The preceding alcohol (39.4 mg, 0.223 mmol) and 4a were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7e (69.2 mg, 57 %, 7:1 mixture of E and Z isomers) as a crystalline colorless solid.

$\nu_{\text{max}} / \text{cm}^{-1}$: (solid) 2970 (m), 2920 (m), 1784 (s), 1655 (m), 1598 (m), 1494 (s), 1167 (s).

**Spectroscopic data for the major E isomer:**

$\delta_H$ (400 MHz, CDCl$_3$) 7.76 (2H, d, $J = 8.5$ Hz, Ts ArCH), 7.35 (2H, d, $J = 8.5$ Hz, Ts ArCH), 7.30 – 7.23 (2H, m, ArCH), 7.21 – 7.13 (3H, m, ArCH), 5.60 (1H, dt, $J = 15.0$, 6.5 Hz, C5-H), 5.43 (1H, dt, $J = 15.0$, 7.0 Hz, C4-H), 3.31 (2H, d, $J = 6.5$ Hz, C6-H2), 3.20 (2H, br s, C1-H2), 2.45 (3H, s, Ts CH$_3$), 2.17 (2H, dt, $J = 7.0$, 7.0 Hz, C3-H2), 1.65 (2H, tt, $J = 7.0$, 7.0 Hz, C2-H2).
$\delta^{13}$C (101 MHz, CDCl$_3$) 146.0 (Ts ArC), 140.8 (ArC), 130.8 (C5), 130.2 (Ts ArC), 130.0 (Ts ArCH), 129.9 (C4), 129.7 (Ts ArCH), 128.6 (ArCH), 128.5 (ArCH), 126.1 (ArCH), 52.2 (C1), 39.1 (C6), 29.3 (C3), 26.5 (C2), 21.9 (Ts CH$_3$).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta$F (377 MHz, CDCl$_3$) -135.9 – -136.0 (2F, m), -146.1 (1F, tt, $J = 21.0, 5.5$ Hz), -158.9 – -159.1 (2F, m).

Characteristic signals for the minor Z isomer:

$\delta$H (400 MHz, CDCl$_3$) 3.40 (2H, d, $J = 7.5$ Hz), 2.32 (2H, q, $J = 7.0$ Hz).

HRMS: (ESI$^+$) Calculated for C$_{26}$H$_{22}$F$_5$NNaO$_4$S: 562.1082. Found [M+Na]$^+$: 562.1072.

(E)-2-Methylbut-2-en-1-ol

General procedure D: Tiglic acid (15.0 g, 150 mmol) was employed, using anhydrous Et$_2$O as the solvent and 1.1 eq. LiAlH$_4$ (1M in Et$_2$O). The title compound (10.8 g, 84 %) was isolated as a colorless oil.

The spectroscopic properties were consistent with the data available in the literature.$^9$

(E)-1-Bromo-2-methylbut-2-ene

General procedure E: The preceding allylic alcohol (10.4 g, 121 mmol) was employed, the title compound (11.6 g, 63 %) was isolated as a colorless oil.

The spectroscopic properties were consistent with the data available in the literature.$^{10}$

(E)-4-Methylhex-4-enoic acid
General procedure C: The preceding allylic bromide (1.18 ml, 10.0 mmol) was employed, the crude product was used in the next step without further purification.

The $^1$H NMR spectrum was consistent with the data available in the literature.$^{11}$

(E)-4-Methylhex-4-en-1-ol

General procedure D: The preceding crude carboxylic acid was employed, using anhydrous Et$_2$O as the solvent and 2.0 eq. LiAlH$_4$ (1M in Et$_2$O). The crude mixture was purified by FCC (eluent 4:1 pentane:Et$_2$O) to afford the title compound (618 mg, 54 % over two steps) as a pale yellow oil.

$\nu_{\text{max}} / \text{cm}^{-1}$: (film) 3327 (br s), 2936 (s), 2863 (s), 1444 (s), 1381 (s), 1059 (s).

$\delta_h$ (400 MHz, CDCl$_3$) 5.28 – 5.22 (1H, m), 3.63 (2H, t, $J = 6.5$ Hz), 2.09 – 2.03 (2H, m), 1.71 – 1.63 (2H, m), 1.61 (3H, t, $J = 1.0$ Hz), 1.57 (3H, dq, $J = 6.5$, 1.0 Hz), 1.34 (1H, br s, OH).

$\delta_c$ (101 MHz, CDCl$_3$) 135.6, 119.0, 63.1, 36.1, 30.9, 15.7, 13.5.

The spectroscopic properties were consistent with the data available in the literature.$^{12}$

(E)-N-4-Methylhex-4-en-1-yl-N-(pentafluorobenzoyloxy)-methanesulfonamide (7f)

General procedure B: The preceding alcohol (54.2 mg, 0.475 mmol) and 4b were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7f (121 mg, 63 %) as a crystalline colorless solid.

m.p. 67-68 °C (Et$_2$O:hexane, plates)

$\nu_{\text{max}} / \text{cm}^{-1}$: (solid) 2936 (m), 1780 (s), 1653 (m), 1502 (s), 1354 (s), 1163 (s).
δ_H (400 MHz, CDCl_3) 5.26 (1H, q, J = 6.5 Hz, C5-H), 3.43 (2H, br s, C1-H), 3.04 (3H, s, Ms CH_3), 2.15 (2H, t, J = 7.5 Hz, C3-H), 1.78 (2H, tt, J = 7.5 Hz, C2-H), 1.61 – 1.56 (6H, m, C6-H and C7-H).

δ_C (101 MHz, CDCl_3) 133.9 (C4), 120.2 (C5), 52.2 (C1), 36.3 (C3), 34.5 (Ms CH_3), 25.1 (C2), 15.5 (C7), 13.5 (C6).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

δ_F (377 MHz, CDCl_3) -135.8 – -135.9 (2F, m), -145.3 (1F, tt, J = 21.0, 5.5 Hz), -158.8 – -159.0 (2F, m).


Cyclohex-1-en-ylmethanol

To a solution of methyl 1-cyclohexene-1-carboxylate (5.00 g, 35.6 mmol) in anhydrous DCM (approx. 100 mL) at -78 °C was added diisobutyl aluminium hydride (1.0 M in DCM, 78 mL, 78 mmol). The reaction mixture was stirred at this temperature for 2 hours before addition of MeOH (70 mL) and saturated aqueous Rochelle’s salt (70 mL). The mixture was warmed to room temperature and stirred overnight before the resulting phases were separated and the aqueous phase extracted with EtOAc (2 × 100 mL). The EtOAc extracts were washed with brine (100 mL) and saturated aqueous Rochelle’s salt (100 mL), dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by FCC (gradient elution 8:1 – 4:1 hexane:EtOAc) to afford the title compound (3.98 g, 100 %) as a colorless oil.

The spectroscopic properties were consistent with the data available in the literature.¹⁰

1-(Bromomethyl)cyclohex-1-ene
General procedure E: The preceding allylic alcohol (3.50 g, 31.1 mmol) was employed to afford the title compound (4.26 g, 78 %) as a colorless oil.

The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{10}

3-(Cyclohex-1-en-yl)propanoic acid

\begin{center}
\includegraphics[width=0.2\textwidth]{cyclohex-1-en-ylpropanoic_acid.png}
\end{center}

General procedure C: The preceding allylic bromide (1.36 mL, 10.0 mmol) was employed, the crude product was used in the next step without further purification.

The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{13}

3-(Cyclohex-1-en-yl)propan-1-ol

\begin{center}
\includegraphics[width=0.2\textwidth]{cyclohex-1-en-ylpropan-1-ol.png}
\end{center}

General procedure D: The preceding crude carboxylic acid was employed, using anhydrous THF as the solvent and 1.5 eq. LiAlH\textsubscript{4} (1M in Et\textsubscript{2}O). The crude mixture was purified by FCC (eluent 4:1 hexane:EtOAc) to afford the title compound (1.26 g, 90 % over two steps) as a pale yellow oil.

\[ \nu_{\text{max}} / \text{cm}^{-1}: \text{film} \ 3326 \ (\text{br s}), 2923 \ (s), 2834 \ (s), 1438 \ (m), 1058 \ (s). \]

\[ \delta_{H} (400 \text{ MHz, CDCl}_{3}) \ 5.44 - 5.40 \ (1H, \text{ m}), 3.61 \ (2H, \text{ t, } J = 6.5 \text{ Hz}), 2.02 - 1.88 \ (6H, \text{ m}), 1.74 \ (1H, \text{ s}), 1.69 - 1.48 \ (6H, \text{ m}). \]

\[ \delta_{C} (101 \text{ MHz, CDCl}_{3}) \ 137.5, 121.4, 63.0, 34.5, 30.6, 28.3, 25.3, 23.1, 22.6. \]

The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{13}

N-3-(Cyclohex-1-en-yl)propan-1-yl-N-(pentafluorobenzoyloxy)-methanesulfonamide (7g)
**General procedure B:** The preceding alcohol (76.1 mg, 0.543 mmol) and 4b were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7g (121 mg, 52 %) as a crystalline colorless solid.

m.p. 98-99 °C (Et2O:hexane, needles)

$\nu_{\text{max}}$ / cm$^{-1}$: (solid) 3023 (m), 2932 (m), 1779 (m), 1651 (m), 1501 (s), 1323 (s), 1162 (s).

$\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 5.46 – 5.41 (1H, m, C5-H), 3.45 (3H, br t, $J$ = 7.0 Hz, C1-H$_2$), 3.04 (3H, s, Ms CH$_3$), 2.10 (2H, t, $J$ = 7.5 Hz, C3-H$_2$), 2.01 – 1.94 (2H, m, C6-H$_2$), 1.92 – 1.87 (2H, m, C9-H$_2$), 1.78 (2H, tt, $J$ = 7.5, 7.0 Hz, C2-H$_2$), 1.65 – 1.58 (2H, m, C7-H$_2$), 1.58 – 1.50 (2H, m, C8-H$_2$).

$\delta_{\text{C}}$ (101 MHz, CDCl$_3$) 136.0 (C4), 122.5 (C5), 52.3 (C1), 34.7 (C3), 34.6 (Ms CH$_3$), 28.2 (C9), 25.3 (C6), 24.9 (C2), 23.0 (C8), 22.6 (C7).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta_{\text{F}}$ (377 MHz, CDCl$_3$) -135.8 – -136.0 (2F, m), -145.3 (1F, tt, $J$ = 21.0, 5.5 Hz), -158.7 – -158.9 (2F, m).

HRMS: (ESI$^+$) Calculated for C$_{17}$H$_{18}$F$_5$NNaO$_4$S: 450.0769. Found [M+Na]$^+$: 450.0769.

**2-Benzylacrylaldehyde**

\[ \text{Ph} \quad \text{C} = \text{C} \quad \text{H} \]

This compound was prepared according to a literature procedure.$^{14}$

The spectroscopic properties were consistent with the data available in the literature.$^{14}$

**3-Benzylbut-3-en-2-ol**

\[ \begin{array}{c}
\text{Ph} \\
\text{5} \\
\text{4} \\
\text{Me} \\
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{H} \\
\text{J} \\
\text{1} \\
\end{array} \]
To a solution of MeLi (1.6 M in Et₂O, 16.0 mL, 25.6 mmol) in anhydrous THF (20 mL) at 0 °C was added a solution of the preceding aldehyde (2.50 g, 17.1 mmol) in anhydrous THF (15 mL) dropwise. The reaction mixture was stirred for 1 hour at room temperature before addition of saturated aqueous NH₄Cl (50 mL). The resulting phases were separated and the aqueous phase extracted with Et₂O (2 × 50 mL), the organic phases were dried over Na₂SO₄ and concentrated in vacuo to afford the title compound (2.67 g, 96%) as a pale yellow oil.

ν_max / cm⁻¹: (film) 3349 (br s), 3027 (m), 2975 (m), 1647 (m), 1453 (m), 1070 (s).

δ_H (400 MHz, CDCl₃) 7.33 – 7.27 (2H, m, ArCH), 7.24 – 7.19 (3H, m, ArCH), 5.16 – 5.14 (1H, m, C₄-H), 4.75 (1H, d, J = 1.5 Hz, C₄-H'), 4.26 (1H, q, J = 6.5 Hz, C₂-H), 3.48 (1H, d, J = 15.5 Hz, C₅-H), 3.36 (1H, d, J = 15.5 Hz, C₅-H'), 1.52 (1H, br s, OH), 1.31 (3H, d, J = 6.5 Hz, C₁-H₃).

δ_C (101 MHz, CDCl₃) 152.7 (C₃), 139.5 (ArC), 129.3 (ArCH), 128.5 (ArCH), 126.3 (ArCH), 111.0 (C₄), 70.3 (C₂), 39.1 (C₅), 22.4 (C₁).


Ethyl (Z)-4-benzylhex-4-enoate

General procedure F: The preceding allylic alcohol (2.43 g, 15.0 mmol) was employed, FCC (eluent 29:1 hexane:EtOAc) afforded title compound (2.98 g, 86%) as a colorless oil.

ν_max / cm⁻¹: (film) 3027 (m), 2978 (m), 2920 (m), 1732 (s), 1602 (m), 1494 (m), 1452 (s), 1164 (s).

δ_H (400 MHz, CDCl₃) 7.30 – 7.24 (2H, m, ArCH), 7.21 – 7.13 (3H, m, ArCH), 5.45 (1H, q, J = 6.5 Hz, C₅-H), 4.09 (2H, q, J = 7.0 Hz, OCH₂CH₃), 3.42 (2H, s, C₇-H₂), 2.39 – 2.31 (2H, m, C₂-H₂), 2.29 – 2.23 (2H, m, C₃-H₃), 1.72 (3H, d, J = 6.5 Hz, C₆-H₃), 1.22 (3H, t, J = 7.0 Hz, OCH₂CH₃).

δ_C (101 MHz, CDCl₃) 173.5 (C₁), 140.0 (ArC), 137.0 (C₄), 128.6 (ArCH), 128.5 (ArCH), 126.1 (ArCH), 121.1 (C₅), 60.3 (OCH₂CH₃), 35.8 (C₇), 33.2 (C₂), 31.9 (C₃), 14.4 (OCH₂CH₃), 13.8 (C₆).

(Z)-4-Benzylhex-en-1-ol

General procedure D: The preceding ester (1.50 g, 6.46 mmol) was employed, using anhydrous THF as the solvent and 0.8 eq. LiAlH₄ (1M in THF). The crude mixture was purified by FCC (eluents 4:1 hexane:EtOAc) afforded the title compound (1.12 g, 91 %) as a colorless oil.

νmax / cm⁻¹: (film) 3330 (br s), 3026 (m), 2929 (m), 1601 (m), 1452 (m), 1055 (s).

δH (400 MHz, CDCl₃) 7.33 – 7.24 (2H, m, ArCH), 7.22 – 7.12 (3H, m, ArCH), 5.46 (1H, q, J = 7.0 Hz, C₅-H), 3.58 (2H, t, J = 6.5 Hz, C₁-H₂), 3.42 (2H, s, C₇-H₂), 2.02 – 1.97 (2H, m, C₃-H₂), 1.73 (3H, d, J = 7.0 Hz, C₆-H₃), 1.68 – 1.60 (2H, m, C₂-H₂), 1.35 (1H, s, O-H).

δC (101 MHz, CDCl₃) 140.3 (ArC), 138.2 (C₄), 128.6 (ArCH), 128.5 (ArCH), 126.0 (ArCH), 120.7 (C₅), 62.9 (C₁), 35.7 (C₇), 32.9 (C₃), 31.0 (C₂), 13.8 (C₆).


(Z)-N-4-Benzylhex-en-1-yl-N-(pentafluorobenzoyloxy)-methanesulfonamide (7h)

General procedure B: The preceding alcohol (90.4 mg, 0.475 mmol) and 4b were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7h (124 mg, 55 %) as a crystalline colorless solid.

m.p. 82-83 °C (Et₂O:hexane, needles)

νmax / cm⁻¹: (solid) 3028 (m), 2934 (m), 1780 (s), 1655 (m), 1597 (m), 1499 (s), 1169 (s).
δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 7.27 – 7.22 (2H, m, ArCH\textsubscript{3}), 7.18 – 7.13 (3H, m, ArCH), 5.48 (1H, q, J = 7.0 Hz, C5-H), 3.43 – 3.33 (4H, m, C1-H\textsubscript{2} and C7-H\textsubscript{2}), 3.00 (3H, s, MS CH\textsubscript{3}), 2.10 (2H, t, J = 7.0 Hz, C3-H\textsubscript{2}), 1.77 – 1.68 (5H, m, C2-H\textsubscript{2} and C6-H\textsubscript{3}).

δ\textsubscript{C} (101 MHz, CDCl\textsubscript{3}) 140.0 (ArC), 136.8 (C4), 128.6 (ArCH), 128.5 (ArCH), 126.0 (ArCH), 122.0 (C5), 52.2 (C1), 35.7 (C7), 34.5 (MS CH\textsubscript{3}), 33.5 (C3), 25.2 (C2), 13.9 (C6).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

δ\textsubscript{F} (377 MHz, CDCl\textsubscript{3}) -135.7 – -135.9 (2F, m), -145.3 (1F, tt, J = 20.5, 5.5 Hz), -158.7 – -158.9 (2F, m).

HRMS: (ESI\textsuperscript{+}) Calculated for C\textsubscript{21}H\textsubscript{20}F\textsubscript{5}NNaO\textsubscript{4}S: 500.0925. Found [M+Na]\textsuperscript{+}: 500.0919.

\textit{(E)-4-Phenylbut-3-en-2-ol}

\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{Me} & 
\end{align*}
\]

To a solution of cinnamaldehyde (10.0 g, 75.6 mmol) in anhydrous Et\textsubscript{2}O (approx. 250 mL) at 0 °C was added MeLi (1.6 M in Et\textsubscript{2}O, 56.7 mL, 90.7 mmol). The reaction mixture was stirred for 2 hours at room temperature before addition of water (10 mL) followed by saturated aqueous NH\textsubscript{4}Cl (150 mL). The resulting phases were separated and the aqueous phase extracted with Et\textsubscript{2}O (2 × 100 mL), the organic phases were dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated \textit{in vacuo}. FCC (eluent 4:1 hexane:EtOAc) afforded the title compound (8.87 g, 79 %) as a yellow oil.

The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{15}

\textbf{Ethyl (E)-3-phenylhex-4-enoate}

\[
\begin{align*}
\text{Me} & \quad \text{Ph} \quad \text{O} \\
\text{Et} & 
\end{align*}
\]

\textbf{General procedure F:} The preceding allylic alcohol (2.00 g, 13.5 mmol) was employed. FCC (gradient elution 49:1 – 9:1 hexane:EtOAc) afforded the title compound (1.75 g, 59 %) as a colorless oil.
The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{16}

\textbf{(E)-3-Phenylhex-4-en-1-ol}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [shape=circle,draw=black,inner sep=1pt]{Me};
\node at (1,0) [shape=circle,draw=black,inner sep=1pt]{Ph};
\node at (2,0) [shape=circle,draw=black,inner sep=1pt]{\text{OH}};
\end{tikzpicture}
\end{center}

\textbf{General procedure D:} The preceding ester (1.67 g, 7.65 mmol) was employed, using anhydrous THF as the solvent and 1.2 eq. LiAlH\textsubscript{4} (1M in THF). The crude mixture was purified by FCC (gradient elution 7:1 – 4:1 hexane:EtOAc) to afford the title compound (480 mg, 36 \%) as a colorless oil.

$\delta$\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 7.33 – 7.28 (2H, m), 7.23 – 7.17 (3H, m), 5.60 (1H, ddq, $J$ = 15.0, 8.0, 1.5 Hz), 5.56 – 5.46 (1H, m), 3.67 – 3.57 (2H, m), 3.41 (1H, br dt, $J$ = 8.0 Hz), 2.00 – 1.90 (2H, m), 1.68 (3H, ddd, $J$ = 5.5, 1.5, 1.0 Hz), 1.42 (1H, br s).

$\delta$\textsubscript{C} (101 MHz, CDCl\textsubscript{3}) 144.8, 134.8, 128.7, 127.6, 126.3, 125.3, 61.3, 45.6, 38.8, 18.1.

\textit{The spectroscopic properties were consistent with the data available in the literature.}\textsuperscript{17}

\textbf{(E)-N-3-Phenylhex-4-en-1-yl-N-(pentafluorobenzoyloxy)-4-toluenesulfonamide (7i)}

\begin{center}
\begin{tikzpicture}
\node at (0,0) [shape=circle,draw=black,inner sep=1pt]{Me};
\node at (1,0) [shape=circle,draw=black,inner sep=1pt]{Ph};
\node at (2,0) [shape=circle,draw=black,inner sep=1pt]{\text{OFBz}};
\end{tikzpicture}
\end{center}

\textbf{General procedure B:} The preceding alcohol (23.3 mg, 0.132 mmol) and 4a were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7i (58.7 mg, 83 \%) as a crystalline colorless solid.

m.p. 121-122 °C (Et\textsubscript{2}O:hexane, \textit{cubes})

$\nu$\textsubscript{max} / cm\textsuperscript{-1}: (solid) 2907 (m), 1780 (s), 1656 (m), 1596 (m), 1505 (s), 1171 (s).

$\delta$\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 7.76 (2H, d, $J$ = 8.0 Hz, Ts ArCH), 7.36 (2H, d, $J$ = 8.0 Hz, Ts ArCH), 7.32 – 7.25 (2H, m, ArCH), 7.21 – 7.15 (3H, m, ArCH), 5.59 – 5.46 (2H, m, C4-H and C5-H), 3.53 (1H, dt, $J$ = 7.0, 6.0 Hz, C3-H), 3.18 (2H, br s, C1-H\textsubscript{2}), 2.46 (3H, s, Ts CH\textsubscript{3}), 1.89 (2H, dt, $J$ = 7.0, 7.0 Hz, C2-H\textsubscript{2}), 1.66 (3H, d, $J$ = 4.5 Hz, C6-H\textsubscript{3}).
$\delta_c$ (101 MHz, CDCl$_3$) 146.0 (Ts ArC), 144.0 (ArC), 133.3 (C4 or C5), 130.2 (Ts ArC), 130.0 (Ts ArCH), 129.8 (Ts ArCH), 128.8 (ArCH), 127.6 (ArCH), 2 x 126.5 (ArCH and C4 or C5), 50.9 (C1), 45.6 (C3), 33.0 (C2), 21.9 (Ts CH$_3$), 18.1 (C6).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta_f$ (283 MHz, CDCl$_3$) -135.7 – -136.0 (2F, m), -146.0 (1F, tt, J = 21.0, 5.0 Hz), -158.8 – -159.2 (2F, m).

HRMS: (ESI$^+$) Calculated for C$_{26}$H$_{22}$F$_5$NNaO$_4$: 562.1082. Found [M+Na$^+$]: 562.1077.

(E)-Hex-4-enal

This compound was prepared according to a literature procedure.$^{18}$

The spectroscopic properties were consistent with the data available in the literature.$^{18}$

(E)-1-Cyclopropylhex-4-en-1-ol

To a suspension of Mg turnings (413 mg, 17.0 mmol) activated with a few crystals of iodine in anhydrous Et$_2$O (15 mL) was added bromocyclopropane (1.28 mL, 16.0 mmol). The reaction mixture was heated to reflux and diluted with more Et$_2$O (20 mL). After 2 hours the reaction mixture was cooled to room temperature before addition of a solution of (E)-hex-4-enal (981 mg, 10.0 mmol) in anhydrous Et$_2$O (10 mL). The reaction mixture was heated to reflux overnight before addition of saturated aqueous NH$_4$Cl (30 mL). The phases were separated and the aqueous phase extracted with Et$_2$O (2 x 30 mL), the organic phases were dried over Na$_2$SO$_4$ and concentrated in vacuo, FCC (gradient elution, 5:1 – 3:1 pentane:Et$_2$O) afforded the title compound (993 mg, 71 %) as a pale yellow oil.

$\nu_{\text{max}}$ / cm$^{-1}$: (film) 3362 (m), 3080 (m), 2924 (s), 1435 (s), 1042 (s).

25
δ_H (400 MHz, CDCl_3) 5.51 – 5.38 (2H, m, C6-H and C7-H), 2.91 – 2.82 (1H, m, C3-H), 2.22 – 2.04 (2H, m, C5-H2), 1.69 – 1.61 (5H, m, C4-H2 and C8-H3), 1.56 (1H, br s, OH), 0.89 (1H, dt, J = 8.5, 8.5, 5.0 Hz, C2-H), 0.56 – 0.45 (2H, m, C1-H), 0.31 – 0.16 (2H, m, C1'-H).

δ_C (101 MHz, CDCl_3) 131.2 (C6 or C7), 125.3 (C6 or C7), 76.5 (C3), 37.1 (C4), 29.0 (C5), 18.1 (2 signals, C2 and C8), 2.8 (C1), 2.6 (C1').

HRMS: (EI') Calculated for C_{9}H_{14}: 122.1096. Found [M-H_2O]^+: 122.1100.

(E)-N-1-Cyclopropylhex-4-en-1-yl-N-(pentafluorobenzoyloxy)-4-toluenesulfonamide (7j)

General procedure B: The preceding alcohol (66.6 mg, 0.475 mmol) and 4a were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7j (203 mg, 85 %) as a colorless oil.

ν_max / cm⁻¹: (film) 2929 (m), 1786 (s), 1653 (m), 1598 (m), 1498 (s), 1325 (s), 1165 (s).

δ_H (500 MHz, CDCl_3) 7.85 (2H, d, J = 8.0 Hz, ArCH), 7.35 (2H, d, J = 8.0 Hz, ArCH), 5.53 – 5.43 (1H, m, C7-H), 5.42 – 5.32 (1H, m, C6-H), 3.53 – 3.33 (1H, m, C3-H), 2.47 (3H, s, Ts C_H3), 2.38 – 2.14 (2H, m, C5-H2), 1.80 – 1.64 (5H, m, C4-H2 and C8-H3), 1.05 (1H, br s, C2-H), 0.67 (1H, br s, C1-H), 0.63 – 0.54 (2H, m, C1-H' and C1'-H'), 0.34 (1H, br s, C1'H).

δ_C (126 MHz, CDCl_3) 156.4 (Bz CH=O), 145.6 (ArC), 133.5 (ArC), 130.2 (C6), 129.8 (ArCH), 129.5 (ArCH), 126.1 (C7), 67.3 (C3), 32.8 (C4), 29.4 (C5), 21.9 (Ts CH3), 18.1 (C8), 13.0 (C2), 5.8 (2 signals, C1 and C1').

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

δ_F (377 MHz, CDCl_3) -136.3 – -136.5 (2F, m), -146.3 (1F, tt, J = 21.0, 5.0 Hz), -158.9 – -159.1 (2F, m).

HRMS: (ESI') Calculated for C_{23}H_{22}F_{8}NNaO_{2}S: 526.1082. Found [M+Na]^+: 526.1087.
(E)-1-Phenylhex-4-ene-1-one

\[ \text{Ph} \quad \begin{array}{c} \text{O} \\ \text{Me} \end{array} \]

To a suspension of NaH (60 % weight in mineral oil, 1.12 g, 28.0 mmol) in anhydrous THF (approx. 60 mL) at 0 °C was added ethyl benzoylacetate (4.85 mL, 28.0 mmol) dropwise. The reaction mixture was stirred at room temperature for 1 hour before dropwise addition of crotol bromide (2.06 mL, 20.0 mmol). After 16 hours the reaction mixture was concentrated in vacuo and the mono- and bis-alkylated products were separated by FCC (gradient elution, 24:1 – 19:1 hexane:EtOAc) to afford a mixture of mono-alkylated dicarbonyl and unconsumed ethyl benzoylacetate (3.48 g). This mixture was hydrolyzed in a solution of KOH (4.1 g, 78 mmol) in water:MeOH (1:1, 40 mL) for 6 hours before addition of 10 M aqueous HCl (16 mL, 160 mmol). The reaction mixture was concentrated to an aqueous solution before being extracted with EtOAc (3 x 60 mL). The organic phases were dried over Na$_2$SO$_4$, concentrated in vacuo and the crude mixture was purified by FCC (eluent 40:1 hexane:EtOAc) to afford the title compound (1.15 g, 33 %) as a colorless oil.

The spectroscopic properties were consistent with the data available in the literature.$^{19}$

(E)-1-Phenylhex-4-ene-1-ol

\[ \text{Ph} \quad \begin{array}{c} \text{OH} \\ \text{Me} \end{array} \]

To a solution of preceding ketone (741 mg, 4.25 mmol) in MeOH (30 mL) at 0 °C was added NaBH$_4$ (241 mg, 6.38 mmol), the reaction mixture was stirred at this temperature for 1 hour before addition of water (20 mL) and extraction with DCM (3 x 30 mL). The DCM extracts were dried over Na$_2$SO$_4$, concentrated in vacuo and filtered through a short plug of silica. The filtrate was concentrated in vacuo to afford the title compound (708 mg, 95 %) as a colorless oil.

\(\delta_H\) (400 MHz, CDCl$_3$) 7.37 – 7.32 (4H, m), 7.31 – 7.24 (1H, m), 5.52 – 5.39 (2H, m), 4.68 (1H, ddd, \(J = 7.5, 5.5, 3.5\) Hz), 2.17 – 1.99 (2H, m), 1.98 – 1.94 (m, 1H), 1.91 – 1.71 (2H, m), 1.67 – 1.63 (3H, m).

The spectroscopic properties were consistent with the data available in the literature.²⁰

(E)-N-1-Phenylhex-4-ene-1-yl-N-(pentafluorobenzoyloxy)-methanesulfonamide (7k)

General procedure B: The preceding alcohol (12 mg, 0.068 mmol) and 4b were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7k (33.9 mg, 62 %) as a crystalline colorless solid.

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.


(E)-Dec-8-en-5-ol

To a solution of n-BuLi (1.55 M in hexane, 10.0 mL, 15.5 mmol) in anhydrous THF (30 mL) at 0 °C was added a solution of (E)-hex-4-enal (1.40 g, 14.3 mmol) in anhydrous THF (5 mL) dropwise. The
reaction mixture was stirred for 1 hour before addition of saturated aqueous NH₄Cl (25 mL), the resulting phases were separated and the aqueous phase was extracted with Et₂O (2 x 40 mL). The organic phases were dried over Na₂SO₄ and concentrated in vacuo to afford the title compound (1.75 g, 78 %) as a pale yellow oil.

ν max / cm⁻¹: (film) 3344 (br s), 2930 (s), 2858 (s), 1482 (s), 964 (s).

δH (400 MHz, CDCl₃) 5.52 – 5.40 (2H, m), 3.65 – 3.57 (1H, m), 2.21 – 2.01 (2H, m), 1.65 (3H, d, J = 4.5 Hz), 1.59 – 1.24 (9H, m), 0.91 (3H, t, J = 7.0 Hz).

δC (101 MHz, CDCl₃) 131.1, 125.3, 71.6, 37.2, 37.1, 28.9, 27.8, 22.7, 17.9, 14.1.

The spectroscopic properties were consistent with the data available in the literature.²¹

(E)-N-Dec-8-en-5-yl-N-(pentafluorobenzyloxy)-methanesulfonamide (7l)

General procedure B: The preceding alcohol (74.2 mg, 0.475 mmol) and 4b were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7l (156 mg, 65 %) as a crystalline colorless solid.

ν max / cm⁻¹: (solid) 2944 (m), 1784 (s), 1651 (m), 1496 (s), 1160 (s).

δH (400 MHz, CDCl₃) 5.54 – 5.44 (1H, m, C9-H), 5.43 – 5.34 (1H, m, C8-H), 3.98 (1H, tt, J = 6.5, 6.5 Hz, C5-H), 3.09 (3H, s, Ms CH₃), 2.30 – 2.07 (2H, m, C7-H₂), 1.75 – 1.23 (11H, m, C2-H₂, C3-H₂, C4-H₂, C6-H₂ and C10-H₃), 0.91 (3H, t, J = 7.0 Hz, C1-H₃).

δC (101 MHz, CDCl₃) 129.9 (C8), 126.4 (C9), 62.3 (C5), 40.0 (Ms CH₃), 31.8 (C2, C3, C4 or C6), 31.5 (C2, C3, C4 or C6), 29.5 (C7), 28.7 (C2, C3, C4 or C6), 22.6 (C2, C3, C4 or C6), 18.1 (C10), 14.0 (C1).

The signals corresponding to the pentafluorobenzyloxy group could not be resolved due to their weak intensity.

δF (377 MHz, CDCl₃) -135.9 – -136.1 (2F, m), -145.4 (1F, tt, J = 21.0, 5.5 Hz), -158.6 – -158.8 (2F, m).

HRMS: (ESI⁺) Calculated for C₁₈H₂₂F₅N₃NaO₄S: 466.1082. Found [M+ Na⁺]: 466.1070.
Methyl 3-cyclopropyl-3-oxopropanoate

This compound was prepared according to a literature procedure.\textsuperscript{10}

The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{10}

Methyl (E)-2-(cyclopropanecarbonyl)-4-methylhex-4-enoate

To a suspension of NaH (60\% weight in mineral oil, 720 mg, 18.0 mmol) in anhydrous DMF (35 mL) was added the preceding \(\beta\)-keto ester (2.31 mL, 18.0 mmol) dropwise. The reaction mixture was stirred at room temperature for 1 hour before addition of (E)-1-bromo-2-methylbut-2-ene (1.42 mL, 12.0 mmol) and heated to 80 °C overnight. The reaction mixture was cooled to room temperature before addition of saturated aqueous NH\(_4\)Cl (50 mL) and extraction with Et\(_2\)O (3 \times 50 mL). The organic phases were dried over Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo}, the crude mixture was purified by FCC (gradient elution 19:1 – 14:1 hexane:EtOAc) to afford the title compound (2.01 g, 80\%) as a colorless oil.

\(\nu_{\text{max}}/\text{cm}^{-1}\): (film) 2954 (m), 1740 (s), 1701 (s), 1436 (s), 1382 (s), 1160 (s).

\(\delta\)H (400 MHz, CDCl\(_3\)) 5.26 (1H, qq, \(J = 7.0, 1.5\) Hz, C\(_7\)-H), 3.77 (1H, t, \(J = 7.5\) Hz, C\(_4\)-H), 3.72 (3H, s, OCH\(_3\)), 2.61 – 2.54 (2H, m, C\(_5\)-H\(_2\)), 2.05 (1H, tt, \(J = 8.0, 4.5\) Hz, C\(_2\)-H), 1.61 (3H, br s, C\(_9\)-H\(_3\)), 1.55 (3H, dq, \(J = 7.0, 1.0\) Hz, C\(_8\)-H\(_3\)), 1.08 – 1.03 (2H, m, C\(_1\)-H), 0.95 – 0.88 (2H, m, C\(_1\)-H\(^+\)).

\(\delta\)C (101 MHz, CDCl\(_3\)) 205.1 (C\(_3\)), 170.2 (C\(_{10}\)), 131.6 (C\(_6\)), 121.4 (C\(_7\)), 58.6 (C\(_4\)), 52.3 (OCH\(_3\)), 38.0 (C\(_5\)), 19.7 (C\(_2\)), 15.5 (C\(_9\)), 13.5 (C\(_8\)), 11.8 (C\(_1\)), 11.6 (C\(_1\)-H\(^+\)).

HRMS: (ESI\(^+\)) Calculated for C\(_{12}\)H\(_{18}\)NaO\(_3\): 233.1148. Found [M+Na\(^+\)]: 233.1151.
(E)-1-Cyclopropyl-4-methylhex-4-en-1-ol

To a solution of the preceding β-keto ester (1.94 g, 9.23 mmol) in MeOH:water (5:3, 40 mL) was added KOH (2.07 g, 36.9 mmol). The reaction mixture was stirred at room temperature for 40 minutes before addition of 2 M aqueous HCl (25 mL) and extraction with Et₂O (3 × 70 mL). The organic phases were dried over Na₂SO₄ and concentrated *in vacuo*. The crude mixture was dissolved in EtOAc (30 mL) and heated to reflux for 3 hours before being concentrated *in vacuo*. The resulting oil was dissolved in MeOH (20 mL) and cooled to 0 °C before addition of NaBH₄ (349 mg, 9.23 mmol). The reaction mixture was stirred at this temperature for 2 hours before addition of 1 M aqueous HCl (20 mL) and extraction with Et₂O (3 × 40 mL). The organic phases were dried over Na₂SO₄ and concentrated *in vacuo*, the crude mixture was purified by FCC (eluent 5:2 pentane:Et₂O) to afford the title compound (688 mg, 48 %) as a colorless oil.

ν<sub>max</sub>/ cm<sup>-1</sup>: (film) 3360 (br s), 3080 (m), 2918 (m), 1432 (m), 1019 (s).

δ<sub>H</sub> (400 MHz, CDCl₃) 5.24 (1H, qq, <i>J</i> = 6.5, 1.0 Hz, C<sub>7</sub>-H<sub>1</sub>), 2.84 (1H, ddd, <i>J</i> = 8.5, 7.5, 5.0 Hz, C<sub>3</sub>-H<sub>1</sub>), 2.20 – 2.00 (2H, m, C<sub>5</sub>-H<sub>2</sub>), 1.73 – 1.65 (2H, m, C<sub>4</sub>-H<sub>2</sub>), 1.63 (1H, br s, OH), 1.60 (3H, br s, C<sub>9</sub>-H<sub>3</sub>), 1.56 (3H, dq, <i>J</i> = 6.5, 1.0 Hz, C<sub>8</sub>-H<sub>3</sub>), 0.89 (1H, dtt, <i>J</i> = 8.5, 8.5, 5.0 Hz, C<sub>2</sub>-H<sub>1</sub>), 0.55 – 0.44 (2H, m, C<sub>1</sub>-H<sub>1</sub>), 0.29 – 0.16 (2H, m, C<sub>1</sub>-H<sub>1</sub>‘).

δ<sub>C</sub> (101 MHz, CDCl₃) 135.7 (C<sub>6</sub>), 118.51 (C<sub>7</sub>), 76.6 (C<sub>3</sub>), 35.8 (C<sub>4</sub>), 35.3 (C<sub>5</sub>), 17.9 (C<sub>9</sub>), 15.6 (C<sub>8</sub>), 13.3 (C<sub>2</sub>), 2.7 (C<sub>1</sub>), 2.5 (C<sub>1</sub>‘).

HRMS: (ESI<sup>+</sup>) Calculated for C<sub>10</sub>H<sub>18</sub>NaO: 177.1250. Found [M+Na]<sup>+</sup>: 177.1246.

(E)-N-(1-Cyclopropyl-4-methylhex-4-en-1-yl)-N-(pentafluorobenzoyloxy)-4-toluenesulfonamide
(7m)
**General procedure B:** The preceding alcohol (540 mg, 3.50 mmol) and 4a were employed. FCC (gradient elution, 49:1 – 24:1 hexane:EtOAc) afforded 7m (1.09 g, 60 %) as a pale yellow oil.

ν<sub>max</sub> / cm<sup>-1</sup>: (film) 2926 (m), 1786 (s), 1653 (m), 1598 (m), 1497 (s), 1164 (s).

δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.86 (2H, d, J = 8.0 Hz, ArC<sub>H</sub>), 7.35 (2H, d, J = 8.0 Hz, ArC<sub>H</sub>), 5.25 (1H, br s, C<sub>7</sub>-H), 3.50 – 3.28 (1H, m, C<sub>3</sub>-H), 2.47 (3H, s, Ts C<sub>H</sub>3), 2.39 – 2.13 (2H, m, C<sub>5</sub>-H<sub>2</sub>), 1.85 – 1.69 (2H, m, C<sub>4</sub>-H<sub>2</sub>), 1.63 – 1.54 (6H, m, C<sub>8</sub>-H<sub>3</sub> and C<sub>9</sub>-H<sub>3</sub>), 1.18 – 0.95 (1H, m, C<sub>2</sub>-H), 0.72 – 0.55 (3H, m, C<sub>1</sub>-H and C<sub>1</sub>'-H<sub>2</sub>), 0.33 (1H, br s, C<sub>1</sub>-H').

δ<sub>C</sub> (126 MHz, CDCl<sub>3</sub>) 156.2 (F<sub>Bz</sub>C=O), 145.4 (ArC), 134.7 (C<sub>6</sub>), 133.4 (ArC), 129.6 (ArCH), 129.3 (ArCH), 119.3 (C<sub>7</sub>), 67.4 (C<sub>3</sub>), 36.3 (C<sub>5</sub>), 31.2 (C<sub>4</sub>), 21.7 (Ts C<sub>H</sub>3), 15.5 (C<sub>9</sub>), 13.4 (C<sub>8</sub>), 12.8 (C<sub>2</sub>), 5.7 (C<sub>1</sub>'), 4.8 (C<sub>1</sub>).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

δ<sub>F</sub> (377 MHz, CDCl<sub>3</sub>) -136.3 – -136.5 (2F, m), -146.4 (1F, tt, J = 21.0, 5.0 Hz), -158.9 – -159.1 (2F, m).

HRMS: (ESI<sup>+</sup>) Calculated for C<sub>24</sub>H<sub>24</sub>F<sub>5</sub>NNaO<sub>4</sub>S: 540.1238. Found [M+Na]<sup>+</sup>: 540.1232.

**Methyl (E)-6-hydroxyhex-2-enoate**

![Methyl (E)-6-hydroxyhex-2-enoate](image)

To a solution of Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst (15.7 mg, 25.0 μmol) in anhydrous, degassed DCM (40 mL) was added methyl acrylate (2.25 mL, 25.0 mmol) and pent-4-en-1-ol (0.26 mL, 2.50 mmol). The reaction mixture was heated to reflux overnight before being concentrated in vacuo. The crude mixture was purified by FCC (eluent 2:1 hexane:EtOAc) to afford the title compound (357 mg, 99 %) as a light brown oil (the coloration was due to the presence of trace amounts of Ru-impurities).

ν<sub>max</sub> / cm<sup>-1</sup>: (film) 3417 (br s), 2950 (m), 1720 (s), 1656 (s), 1436 (s), 1272 (s).

δ<sub>H</sub> (400 MHz, CDCl<sub>3</sub>) 6.98 (1H, dt, J = 15.5, 7.0 Hz), 5.85 (1H, dt, J = 15.5, 1.5 Hz), 3.72 (3H, s), 3.67 (2H, t, J = 6.5 Hz), 2.30 (2H, dtd, J = 7.0, 7.0, 1.5 Hz), 1.77 – 1.68 (2H, m), 1.51 (1H, br s).

δ<sub>C</sub> (101 MHz, CDCl<sub>3</sub>) 167.2, 148.9, 121.4, 62.1, 51.6, 31.0, 28.7.
The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{22}

Methyl (E)-6-((N-(pentafluorobenzoyloxy)-4-tolyl)sulfonamido)hex-2-enoate (7n)

![Chemical Structure]

**General procedure B:** The preceding alcohol (115 mg, 0.800 mmol) and 4a were employed. FCC (eluuent 49:1 PhMe:EtOAc) afforded 7n (310 mg, 76\%) as a crystalline colorless solid.

$\nu_{\text{max}}$ / cm\(^{-1}\): (solid) 2953 (m), 1790 (s), 1706 (s), 1595 (m), 1501 (s), 1168 (s).

$\delta_H$ (400 MHz, CDCl\(_3\)) 7.79 (2H, d, $J = 8.0$ Hz, ArCH\(_3\)), 7.38 (2H, d, $J = 8.0$ Hz, ArCH\(_2\)), 6.90 (1H, dt, $J = 15.5$, 7.0 Hz, C4-H), 5.85 (1H, dt, $J = 15.5$, 1.5 Hz, C5-H), 3.72 (3H, s, OCH\(_3\)), 3.24 (2H, br s, C1-H\(_2\)), 2.47 (3H, s, Ts CH\(_3\)), 2.42 (2H, tdd, $J = 7.5$, 7.0, 1.5 Hz, C3-H\(_2\)), 1.72 (2H, tt, $J = 7.5$, 7.0 Hz, C2-H\(_2\)).

$\delta_C$ (101 MHz, CDCl\(_3\)) 166.8 (C6), 147.2 (C4), 146.0 (ArC\(_6\)), 129.9 (2 signals, ArC\(_6\) and ArCH\(_3\)), 129.6 (ArCH\(_3\)), 122.1 (C5), 51.8 (C1), 51.5 (OCH\(_3\)), 28.8 (C3), 25.0 (C2), 21.7 (Ts CH\(_3\)).

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta_F$ (377 MHz, CDCl\(_3\)) -135.8 – -136.0 (2F, m), -145.7 (1F, tt, $J = 20.5$, 5.0 Hz), -158.7 – -159.0 (2F, m).

HRMS: (ESI\(^+\)) Calculated for C\(_{21}\)H\(_{18}\)F\(_5\)NNaO\(_6\)S: 530.0667. Found [M+Na\(^+\)]\(^+\): 530.0662.

**Nona-1,8-dien-5-ol**

![Chemical Structure]

This compound was prepared according to a literature procedure.\textsuperscript{23}

$\nu_{\text{max}}$ / cm\(^{-1}\): (film) 3345 (br s), 3078 (m), 2931 (m), 2852 (m), 1641 (m), 1449 (m).
\(\delta_H (400\text{ MHz, CDCl}_3)\) 5.83 (2H, ddt, \(J = 17.0, 10.0, 6.5\text{ Hz}\)), 5.04 (2H, ddt, \(J = 17.0, 1.5, 1.5\text{ Hz}\)), 4.96 (2H, ddt, \(J = 10.0, 1.5, 1.5\text{ Hz}\)), 3.65 (1H, tt, \(J = 7.5, 4.5\text{ Hz}\)), 2.25 – 2.06 (4H, m), 1.91 (1H, s), 1.62 – 1.46 (4H, m).

\(\delta_C (101\text{ MHz, CDCl}_3)\) 138.6, 114.8, 71.0, 36.5, 30.1.

The spectroscopic properties were consistent with the data available in the literature.  

\(N\)-(Nona-1,8-dien-5-yl)-\(N\)-(pentafluorobenzoyloxy)methanesulfonamide

**General procedure B:** The preceding alcohol (28.0 mg, 0.200 mmol) and \(4b\) were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded the title compound (121 mg, 63 %) as a crystalline colorless solid.

\(\nu_{\text{max}} /\text{ cm}^{-1}:\) (film) 2939 (m), 1783 (s), 1653 (m), 1499 (s) 1325 (s), 1161 (s).

\(\delta_H (400\text{ MHz, CDCl}_3)\) 5.78 (2H, ddt, \(J = 17.0, 10.0, 6.5\text{ Hz}\), C4-H), 5.06 (1h, ddt, \(J = 17.0, 1.5, 1.5\text{ Hz}\), C5-H’), 5.03 – 4.98 (2H, m, C5-H), 4.03 (1H, tt, \(J = 6.5, 6.5\text{ Hz}\), C1-H), 3.09 (3H, s, Ms CH3), 2.35 – 2.12 (4H, m, C3-H2), 1.80 – 1.61 (4H, m, C2-H2).

\(\delta_C (101\text{ MHz, CDCl}_3)\) 157.2 (\(^{13}\text{Bz}\ C=O), 137.2 (C4), 115.7 (C5), 61.2 (C1), 39.9 (Ms CH3), 30.8 (C2), 30.4 (C3).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

\(\delta_F (377\text{ MHz, CDCl}_3)\) -135.9 – -136.1 (2F, m), -145.3 (1F, tt, \(J = 21.0, 5.5\text{ Hz}\), -158.6 – -158.8 (2F, m).
To a solution of the preceding compound (63.2 mg, 0.148 mmol) in anhydrous, degassed DCM (80 mL) was added Hoveyda-Grubbs 2nd generation catalyst (2.0 mg, 3.2 μmol). The reaction mixture was heated to reflux overnight before being concentrated in vacuo. The crude mixture was purified by FCC (eluent 1:1 PhMe:hexane) to afford 7o (51.7 mg, 87 %) as a colorless crystalline solid.

$\nu_{\text{max}} / \text{cm}^{-1}$: (solid) 2939 (m), 2845 (m), 1768 (s), 1651 (s), 1591 (s), 1157 (s).

$\delta_H$ (500 MHz, CDCl$_3$) 5.83 – 5.79 (2H, m, C4-H), 4.20 (1H, tt, $J = 10.5, 3.5$ Hz, C1-H), 3.09 (3H, s, Ms CH$_3$), 2.32 – 2.24 (2H, m, C3-H), 2.21 – 2.14 (2H, m, C2-H), 2.12 – 2.04 (2H, m, C3-H'), 1.69 – 1.59 (2H, m, C2-H').

$\delta_C$ (126 MHz, CDCl$_3$) 157.3 ($^1\text{Bz}$ C=O), 131.6 (C4), 65.6 (C1), 39.7 (Ms CH$_3$), 31.0 (C3), 24.8 (C2).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta_F$ (377 MHz, CDCl$_3$) -135.8 – -136.0 (2F, m), -145.2 (1F, tt, $J = 21.0, 5.5$ Hz), -158.5 – -158.7 (2F, m).

HRMS: (ESI$^+$) Calculated for C$_{17}$H$_{18}$F$_5$NaO$_4$S: 450.0769. Found [M+ Na]$^+$: 450.0749.

**N-(Cyclohept-4-en-1-yl)-N-(pentafluorobenzoyloxy)methanesulfonamide (7o)**

To a solution of the preceding compound (63.2 mg, 0.148 mmol) in anhydrous, degassed DCM (80 mL) was added Hoveyda-Grubbs 2nd generation catalyst (2.0 mg, 3.2 μmol). The reaction mixture was heated to reflux overnight before being concentrated in vacuo. The crude mixture was purified by FCC (eluent 1:1 PhMe:hexane) to afford 7o (51.7 mg, 87 %) as a colorless crystalline solid.

$\nu_{\text{max}} / \text{cm}^{-1}$: (solid) 2939 (m), 2845 (m), 1768 (s), 1651 (s), 1591 (s), 1157 (s).

$\delta_H$ (500 MHz, CDCl$_3$) 5.83 – 5.79 (2H, m, C4-H), 4.20 (1H, tt, $J = 10.5, 3.5$ Hz, C1-H), 3.09 (3H, s, Ms CH$_3$), 2.32 – 2.24 (2H, m, C3-H), 2.21 – 2.14 (2H, m, C2-H), 2.12 – 2.04 (2H, m, C3-H'), 1.69 – 1.59 (2H, m, C2-H').

$\delta_C$ (126 MHz, CDCl$_3$) 157.3 ($^1\text{Bz}$ C=O), 131.6 (C4), 65.6 (C1), 39.7 (Ms CH$_3$), 31.0 (C3), 24.8 (C2).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$\delta_F$ (377 MHz, CDCl$_3$) -135.8 – -136.0 (2F, m), -145.2 (1F, tt, $J = 21.0, 5.5$ Hz), -158.5 – -158.7 (2F, m).

HRMS: (ESI$^+$) Calculated for C$_{17}$H$_{18}$F$_5$NaO$_4$S: 450.0769. Found [M+ Na]$^+$: 450.0749.

**Cyclohex-3-en-1-ylmethanol**

To a solution of 3-cyclohexene-1-carboxaldehyde (11.0 g, 100 mmol) in MeOH (150 mL) at 0 °C was added NaBH$_4$ (1.51 g, 40.0 mmol), the reaction mixture was stirred at this temperature for 1 hour before addition of water (100 mL) and extraction with Et$_2$O (3 x 150 mL). The organic phases were
dried over Na$_2$SO$_4$ and concentrated in vacuo, FCC (gradient elution 3:1 – 1:1 pentane:Et$_2$O) afforded the title compound (8.00 g, 71%) as a pale yellow oil.

$\delta$H (400 MHz, CDCl$_3$) 5.70 – 5.62 (2H, m), 3.56 – 3.46 (2H, m), 2.14 – 2.02 (3H, m), 1.86 – 1.67 (4H, m), 1.32 – 1.20 (1H, m).

$\delta$C (101 MHz, CDCl$_3$) 127.2, 126.0, 67.9, 36.4, 28.2, 25.3, 24.7.

The spectroscopic properties were consistent with the data available in the literature.$^{24}$

$N$-(Cyclohex-3-en-1-ylmethyl)-$N$-(pentafluorobenzoyloxy)methanesulfonamide (7p)

**General procedure B:** The preceding alcohol (53.3 mg, 0.475 mmol) and 4b were employed. FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded 7p (100 mg, 53%) as a crystalline colorless solid.

m.p. 109-110 °C (DCM:hexane, needles)

$\nu_{\text{max}}$ / cm$^{-1}$: (solid) 3029 (m), 2917 (m), 1782 (s), 1653 (s), 1505 (s), 1162 (s).

$\delta$H (400 MHz, CDCl$_3$) 5.73 – 5.62 (2H, m, C$_4$-H and C$_5$-H), 3.45 – 3.28 (2H, m, C$_1$-H$_2$), 3.04 (3H, s, Ms CH$_3$), 2.36 – 2.24 (1H, m, C$_3$-H), 2.16 – 2.02 (2H, m, C$_6$-H$_2$), 2.02 – 1.79 (3H, m, C$_2$-H, C$_3$-H’ and C$_7$-H’), 1.50 – 1.38 (1H, m, C$_7$-H’).

$\delta$C (101 MHz, CDCl$_3$) 156.4 (F$_2$Bz C=O), 127.3 (C$_4$ or C$_5$), 125.2 (C$_4$ or C$_5$), 57.7 (C$_1$), 34.2 (Ms CH$_3$), 31.6 (C$_2$), 29.2 (C$_3$), 25.9 (C$_7$), 24.1 (C$_6$).
The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

$$\delta \mathrm{F} \ (377 \text{ MHz, CDCl}_3) \ -135.7 - -135.9 \ (2\text{F, m}), \ -145.3 \ (1\text{F, tt, } J = 21.0, 5.5 \text{ Hz}), \ -158.8 - -159.0 \ (2\text{F, m}).$$

HRMS: (ESI') Calculated for C$_{15}$H$_{14}$F$_5$NNaO$_4$S: 422.0456. Found [M+Na]$^+$: 422.0455.

1-Bromo-2-(prop-1-en-1-yl)benzene

This compound was prepared according to a literature procedure.$^{25}$

$$\nu_{\text{max}} / \text{cm}^{-1} \ (\text{film}) \ 3022 \ (\text{m}), \ 2913 \ (\text{m}), \ 1467 \ (\text{s}), \ 1431 \ (\text{s}), \ 1023 \ (\text{s}).$$

**Spectroscopic data for the major Z isomer:**

$$\delta \mathrm{H} \ (400 \text{ MHz, CDCl}_3) \ 7.61 - 7.56 \ (1\text{H, m, ArCH}), \ 7.33 - 7.21 \ (2\text{H, m, ArCH}), \ 7.14 - 7.07 \ (1\text{H, m, ArCH}), \ 6.49 \ (1\text{H, dq, } J = 11.5, 2.0 \text{ Hz, C1-H}), \ 5.90 \ (1\text{H, dq, } J = 11.5, 7.0 \text{ Hz, C2-H}), \ 1.79 \ (3\text{H, dd, } J = 7.0, 2.0 \text{ Hz, C3-H}).$$

$$\delta \mathrm{C} \ (101 \text{ MHz, CDCl}_3) \ 137.5 \ (\text{ArC}), \ 132.7 \ (\text{ArCH}), \ 130.8 \ (\text{ArCH}), \ 129.5 \ (\text{C1}), \ 128.3 \ (\text{ArCH}), \ 128.2 \ (\text{C2}), \ 126.9 \ (\text{ArCH}), \ 124.2 \ (\text{ArC}), \ 14.5 \ (\text{C3}).$$

**Spectroscopic data for the minor E isomer:**

$$\delta \mathrm{H} \ (400 \text{ MHz, CDCl}_3) \ 7.54 - 7.50 \ (1\text{H, m, ArCH}), \ 7.49 - 7.45 \ (1\text{H, m, ArCH}), \ 7.32 - 7.21 \ (1\text{H, m, ArCH}), \ 7.08 - 7.02 \ (1\text{H, m, ArCH}), \ 6.74 \ (1\text{H, dq, } J = 15.5, 2.0 \text{ Hz, C1-H}), \ 6.19 \ (1\text{H, dq, } J = 15.5, 6.5 \text{ Hz, C2-H}), \ 1.93 \ (3\text{H, dd, } J = 6.5, 2.0 \text{ Hz, C3-H}).$$

$$\delta \mathrm{C} \ (101 \text{ MHz, CDCl}_3) \ 137.8 \ (\text{ArC}), \ 132.9 \ (\text{ArCH}), \ 130.0 \ (\text{C1}), \ 129.0 \ (\text{C2}), \ 128.2 \ (\text{ArCH}), \ 127.5 \ (\text{ArCH}), \ 126.9 \ (\text{ArCH}), \ 123.1 \ (\text{ArC}), \ 18.8 \ (\text{C3}).$$

2-(2-(Prop-1-en-1-yl)phenyl)ethan-1-ol

To a solution of the preceding bromide (2.96 g, 15.0 mmol) in anhydrous THF (40 mL) at -78 °C was added n-BuLi (1.55 M in hexane, 10.6 mL, 16.5 mmol). The reaction mixture was stirred at this temperature for 2 hours before addition ethylene oxide (approx. 3 M in THF, 7.5 mL, 22.5 mmol). The reaction mixture was slowly warmed to room temperature and stirred overnight before addition of saturated aqueous NH₄Cl (30 mL). The resulting phases were separated and the aqueous phase extracted with Et₂O (2 × 40 mL). The organic phases were dried over Na₂SO₄ and concentrated in vacuo, FCC (eluent 3:1 hexane:EtOAc) afforded the title compound (1.50 g, 62 %, 3:1 mixture of Z and E isomers) as a pale yellow oil.

ν_max / cm⁻¹: (film) 3322 (br s), 3017 (m), 2937 (m), 2876 (m), 1484 (s), 1446 (s), 1041 (s).

Spectroscopic data for the major Z isomer:

δ_H (400 MHz, CDCl₃) 7.25 – 7.15 (4H, m, ArCH), 6.55 (1H, dq, J = 11.5, 2.0 Hz, C3-H), 5.86 (1H, dq, J = 11.5, 7.0 Hz, C4-H), 3.78 (2H, t, J = 7.0 Hz, C1-H₂), 2.88 (2H, t, J = 7.0 Hz, C2-H₂), 1.73 (3H, dd, J = 7.0, 2.0 Hz, C5-H₃), 1.46 (1H, br s, OH).

δ_C (101 MHz, CDCl₃) 136.9 (ArC), 136.6 (ArC), 130.0 (2 signals, ArCH), 128.7 (C3), 127.8 (C4), 127.1 (ArCH), 126.3 (ArCH), 63.1 (C1), 36.9 (C2), 14.4 (C5).

Spectroscopic data for the minor E isomer:

δ_H (400 MHz, CDCl₃) 7.46 – 7.41 (1H, m, ArCH), 7.25 – 7.15 (3H, m, ArCH), 6.66 (1H, dq, J = 15.5, 2.0 Hz, C3-H), 6.12 (1H, dq, J = 15.5, 6.5 Hz, C4-H), 3.82 (2H, t, J = 7.0 Hz, C1-H₂), 2.96 (2H, t, J = 7.0 Hz, C2-H₂), 1.91 (3H, dd, J = 6.5, 2.0 Hz, C5-H₃), 1.46 (1H, br s, OH).

δ_C (101 MHz, CDCl₃) 137.5 (ArC), 135.0 (ArC), 130.3 (ArCH), 128.5 (C3), 128.0 (C4), 127.1 (ArCH), 127.0 (ArCH), 126.3 (ArCH), 63.3 (C1), 36.9 (C2), 18.9 (C5).

**N-(2-(Prop-1-en-1-yl)phenethyl)-N-(pentafluorobenzoyloxy)-methanesulfonamide (7q)**

![Chemical structure](image)

**General procedure B:** The preceding alcohol (59.3 mg, 0.366 mmol) was employed with 4b (1.9 eq.), PPh₃ (2.6 eq.) and DEAD (2.6 eq.). FCC (eluent PhMe) afforded 7q (93.9 mg, 57 %) as a crystalline colorless solid.

\[ \nu_{\text{max}} / \text{cm}^{-1}: \text{(solid) } 3024 \text{ (m), } 2943 \text{ (m), } 1787 \text{ (s), } 1653 \text{ (m), } 1498 \text{ (s), } 1165 \text{ (s).} \]

**Spectroscopic data for the major Z isomer:**

\[ \delta_H (400 \text{ MHz, CDCl}_3) 7.26 – 7.10 \text{ (4H, m, ArCH), } 6.49 \text{ (1H, dq, } J = 11.5, 2.0 \text{ Hz, C3-H}), 5.86 \text{ (1H, dq, } J = 11.5, 7.0 \text{ Hz, C4-H}), 3.66 – 3.58 \text{ (2H, m, C1-H2), } 3.05 – 3.02 \text{ (2H, m, C2-H2), } 3.00 \text{ (3H, s, Ms CH}_3\text{), } 1.69 \text{ (3H, dd, } J = 7.0, 2.0 \text{ Hz, C5-H3).} \]

\[ \delta_C (101 \text{ MHz, CDCl}_3) 136.6 \text{ (ArC), } 135.1 \text{ (ArC), } 129.9 \text{ (ArCH), } 129.7 \text{ (ArCH), } 128.4 \text{ (C4), } 127.8 \text{ (C3), } 127.2 \text{ (ArCH), } 126.7 \text{ (ArCH), } 52.7 \text{ (C1), } 34.7 \text{ (Ms CH}_3\text{), } 31.4 \text{ (C2), } 14.3 \text{ (C5).} \]

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

\[ \delta_F (377 \text{ MHz, CDCl}_3) -135.6 – -135.8 \text{ (2F, m), } -144.9 – -145.2 \text{ (1F, m), } -158.6 – -158.8 \text{ (2F, m).} \]

**Spectroscopic data for the minor E isomer:**

\[ \delta_H (400 \text{ MHz, CDCl}_3) 7.41 – 7.37 \text{ (1H, m, ArCH), } 7.24 – 7.13 \text{ (3H, m, ArCH), } 6.59 \text{ (1H, dq, } J = 15.5, 2.0 \text{ Hz, C3-H}), 6.13 \text{ (1H, dq, } J = 15.5, 6.5 \text{ Hz, C4-H}), 3.67 – 3.57 \text{ (2H, m, C1-H2), } 3.13 – 3.08 \text{ (2H, m, C2-H2), } 3.02 \text{ (3H, s, Ms CH}_3\text{), } 1.89 \text{ (3H, dd, } J = 6.5, 2.0 \text{ Hz, C5-H3).} \]

\[ \delta_C (101 \text{ MHz, CDCl}_3) 137.2 \text{ (ArC), } 133.5 \text{ (ArC), } 129.9 \text{ (ArCH), } 128.9 \text{ (C4), } 127.6 \text{ (C3), } 127.4 \text{ (ArCH), } 127.2 \text{ (ArCH), } 126.4 \text{ (ArCH), } 53.1 \text{ (C1), } 34.7 \text{ (Ms CH}_3\text{), } 31.2 \text{ (C2), } 18.7 \text{ (C5).} \]

The signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

\[ \delta_F (377 \text{ MHz, CDCl}_3) -135.6 – -135.8 \text{ (2F, m), } -144.9 – -145.2 \text{ (1F, m), } -158.6 – -158.8 \text{ (2F, m).} \]

2-Methylenehex-5-en-1-ol

\[ \begin{align*}
\text{This compound was prepared according to a literature procedure.}^{26}
\end{align*} \]

*The spectroscopic properties were consistent with the data available in the literature.*\(^{26,27}\)

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**Ethyl 4-methyleneoct-7-enoate**

![Chemical Structure](image)

**General procedure F:** The preceding allylic alcohol (2.24 g, 20.0 mmol) was employed. FCC (eluent 29:1 hexane:EtOAc) afforded the title compound (2.26 g, 62%) as a colorless oil.

\[ \begin{align*}
\nu_{\text{max}} / \text{cm}^{-1} : \text{film} & \text{ 3079 (m), 2981 (s), 2934 (s), 1785 (s), 1445 (s), 1154 (s).} \\
\delta_{\text{H}} (400 \text{ MHz, CDCl}_3) & \text{ 5.80 (1H, ddt, } J = 17.0, 10.5, 6.5 \text{ Hz, C7-H}), 5.02 (1H, ddt, } J = 17.0, 2.0, 1.5 \text{ Hz, C8-H}'), 4.95 (1H, ddt, } J = 10.5, 2.0, 1.0 \text{ Hz, C8-H}), 4.76 (1H, br s, C9-H), 4.74 (1H, br s, C9-H'), 4.12 (2H, q, } J = 7.0 \text{ Hz, OCH}_2\text{CH}_3), 2.47 - 2.42 (2H, m, C2-H2), 2.36 - 2.30 (2H, m, C3-H2), 2.23 - 2.16 (2H, m, C6-H3), 2.14 - 2.08 (2H, m, C5-H3), 1.25 (3H, t, } J = 7.0 \text{ Hz, OCH}_2\text{CH}_3). \\
\delta_{\text{C}} (101 \text{ MHz, CDCl}_3) & \text{ 173.4 (C1), 147.5 (C4), 138.3 (C7), 114.8 (C8), 109.7 (C9), 60.5 (OCH}_2\text{CH}_3), 35.7 (C5), 32.9 (C2), 32.1 (C6), 31.1 (C3), 14.4 (OCH}_2\text{CH}_3). \\
\text{HRMS: (ESI') Calculated for C11H18NaO2: 205.1199. Found [M+Na]^+: 205.1190.}
\end{align*} \]
4-Methyleneoct-7-en-1-ol

General procedure D: The preceding ester (1.00 g, 5.49 mmol) was employed, using anhydrous Et₂O as the solvent and 0.8 eq. LiAlH₄ (1M in Et₂O). The title compound (765 mg, 99 %) was isolated as a colorless oil.

ν max / cm⁻¹: (film) 3323 (br s), 3078 (m), 2932 (s), 1642 (s), 1442 (s), 1057 (s).

δH (400 MHz, CDCl₃) 5.81 (1H, ddt, J = 17.0, 10.0, 6.5 Hz, C7-H), 5.01 (1H, ddt, J = 17.0, 1.5, 1.5 Hz, C8-H'), 4.97 – 4.92 (1H, m, C8-H), 4.76 (1H, br s, C9-H), 4.75 (1H, br s, C9-H'), 3.64 (2H, t, J = 6.5 Hz, C1-H₂), 2.23 – 2.15 (2H, m, C6-H₂), 2.14 – 2.05 (4H, m, C3-H₂ and C5-H₂), 1.77 (1H, br s, OH), 1.70 (2H, tt, J = 7.5, 6.5 Hz, C2-H₂).

δC (101 MHz, CDCl₃) 148.7 (C4), 138.5 (C7), 114.7 (C8), 109.5 (C9), 62.7 (C1), 35.4 (C5), 32.5 (C3), 32.1 (C6), 30.7 (C2).


N-4-Methyleneoct-7-en-1-yl-N-(pentafluorobenzoyloxy)methanesulfonamide (7r)

General procedure B: The preceding alcohol (66.6 mg, 0.475 mmol) and 4b were employed. FCC (eluent 250:1 hexane:EtOAc followed by PhMe) afforded 7r (128 mg, 63 %) as a crystalline colorless solid.

ν max / cm⁻¹: (solid) 3078 (m), 2940 (s), 1782 (s), 1656 (m), 1500 (s), 1355 (s), 1162 (s).

δH (400 MHz, CDCl₃) 5.81 (1H, ddt, J = 17.0, 10.0, 7.0 Hz, C7-H), 5.02 (1H, ddt, J = 17.0, 2.0, 1.0 Hz, C8-H), 4.96 (1H, ddt, J = 10.0, 2.0, 1.0 Hz, C8-H'), 4.80 (1H, s, C9-H), 4.78 (1H, s, C9-H'), 3.48 (2H, t, J = 7.0 Hz, C1-H₂), 3.04 (3H, s, Ms C₃H₅), 2.20 (4H, m, C3-H₂ and C6-H₂), 2.10 (2H, t, J = 7.5 Hz, C5-H₂), 1.82 (2H, tt, J = 7.5, 7.0 Hz, C2-H₂).
\[ \delta_C \text{ (101 MHz, CDCl}_3\text{)} \quad 156.4 \text{ (}^\text{F} \text{Bz C}=\text{O}), \quad 147.3 \text{ (C4), 138.3} \text{ (C7)}, \quad 114.8 \text{ (C8), 110.5} \text{ (C9), 52.2} \text{ (C1),} \\
35.3 \text{ (C5), 34.4 (Ms CH}_3\text{), 32.7} \text{ (C3), 32.0} \text{ (C6), 24.9} \text{ (C2).} \\
\]

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

\[ \delta_F \text{ (377 MHz, CDCl}_3\text{)} \quad -135.8 \text{ –} -136.0 \text{ (2F, m),} -145.2 \text{ (1F, tt, } J = 21.0, 5.5 \text{ Hz),} -158.7 \text{ –} -158.9 \text{ (2F, m).} \]

HRMS: (ESI\textsuperscript{+}) Calculated for C\textsubscript{17}H\textsubscript{18}F\textsubscript{5}SNaO\textsubscript{4}: 450.0769. Found [M+Na]\textsuperscript{+}: 450.0764.

**Catalysis products:**

\textit{N-(4-oxopentyl)-4-toluenesulfonamide (8a')

\[
\text{Me} \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{NHTs}}{\text{N}}
\]

**General procedure G:** Conditions: 3.75 mol \% Pd\textsubscript{2}(dba)_3; 15 mol \% P(3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3}; 200 mol \% Et\textsubscript{3}N; DMF (0.1 M); 120 °C; 2 hours. Substrate 7a (50.0 mg, 0.111 mmol) was employed. FCC (gradient elution, 19:1 – 9:1 – 4:1 – 0:1 hexane:EtOAc) afforded 8a as a colorless oil (23 mg, 81 %).

\[ \nu_{\text{max}} / \text{cm}^{-1}: \text{ (film) 3278 (br s), 2925 (m), 1709 (s), 1598 (m), 1324 (s), 1155 (s), 1092 (s).} \]

\[ \delta_H \text{ (400 MHz, CDCl}_3\text{)} \quad 7.72 \text{ (2H, d, } J = 8.5 \text{ Hz),} 7.29 \text{ (2H, d, } J = 8.5 \text{ Hz),} 4.83 \text{ (1H, t, } J = 6.5 \text{ Hz),} 2.93 \text{ (2H, dt, } J = 6.5, 6.5 \text{ Hz),} 2.50 \text{ (2H, t, } J = 6.5 \text{ Hz),} 2.41 \text{ (3H, s),} 2.11 \text{ (3H, s),} 1.72 \text{ (2H, tt, } J = 6.5, 6.5 \text{ Hz).} \]

\[ \delta_C \text{ (101 MHz, CDCl}_3\text{)} \quad 208.5, 143.6, 137.0, 129.9, 127.2, 42.7, 40.3, 30.2, 23.4, 21.6. \]

HRMS: (ESI\textsuperscript{+}) Calculated for C\textsubscript{12}H\textsubscript{18}NO\textsubscript{3}: 256.1002. Found [M+H]\textsuperscript{+}: 256.1003.

The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{28}
**(3aR*,7aS*)-1-Tosyl-2,3,3a,4,5,7a-hexahydro-1H-indole (8b) and (iso-8b)**

![Diagram of 8b and iso-8b]

**General procedure G:** Conditions: 2.5 mol % Pd(dba)$_3$; 12.5 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 50 mol % Et$_3$N; 6:1 n-BuCN:DMF (0.1 M); 110 °C; 17 hours. Substrate 7ba (68.5 mg, 0.140 mmol) was employed. FCC (9:1 hexane:EtOAc) afforded 8b and iso-8b (35.4 mg, 91 %, 12:1 8b:iso-8b) as a pale yellow oil.

ν$_{max}$/cm$^{-1}$: (film) 3031 (m), 2923 (m), 1598 (m), 1450 (m), 1338 (s), 1157 (s), 1091 (s), 1048 (s).

$^1$H (500 MHz, CDCl$_3$) δ 7.73 (2H, d, J = 8.0 Hz), 7.30 (2H, d, J = 8.0 Hz), 5.83 (1H, dddd, J = 10.5, 2.5, 2.5, 2.5 Hz), 5.80 – 5.72 (1H, m), 3.99 (1H, dd, J = 5.5, 2.5 Hz), 3.47 (1H, ddd, J = 10.0, 7.5, 4.0 Hz), 3.16 (1H, ddd, J = 10.0, 7.5, 7.5 Hz), 2.42 (3H, s), 2.04 – 1.95 (2H, m), 1.95 – 1.87 (1H, m), 1.76 (1H, dddd, J = 12.0, 8.0, 7.5, 7.5 Hz), 1.71 – 1.51 (3H, m).

$^{13}$C (126 MHz, CDCl$_3$) δ 143.3, 135.1, 129.7, 128.4, 127.7, 127.6, 57.6, 47.4, 36.6, 27.8, 23.0, 21.6, 21.0.

The spectroscopic properties were consistent with the data available in the literature.$^{29}$

**Characteristic signals for iso-8b (obtained from 1D TOCSY, irradiated signal at 3.70 ppm):**

δ$^1$H NMR (500 MHz, CDCl$_3$) 5.63 – 5.60 (m), 3.70 (dd, J = 7.5, 7.5, 7.5 Hz, 3.50 – 3.45 (m), 3.12 (dd, J = 10.0, 10.0, 7.5 Hz), 2.53 – 2.45 (m), 2.31 – 2.22 (m), 2.14 – 2.05 (m), 1.97 – 1.91 (m), 1.91 – 1.84 (m), 1.84 – 1.77 (m), 1.76 – 1.69 (m).

HRMS: (ESI$^+$) Calculated for C$_{15}$H$_{20}$NO$_2$S: 278.1209. Found [M+H]$^+$: 278.1207.

**(3aR*,6aS*)-1-Tosyl-1,2,3,3a,4,6a-hexahydrocyclopenta[b]pyrrole (8c)**

![Diagram of 8c]
**General procedure G:** Conditions: 2.5 mol % Pd$_2$(dba)$_3$; 12.5 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 25 mol % Et$_3$N; n-BuCN (0.1 M); 110 °C; 17 hours. Substrate 7c (66.5 mg, 0.140 mmol) was employed. FCC (gradient elution, 9:1 – 4:1 hexane:EtOAc) afforded 8c (33.7 mg, 91%) as a crystalline colorless solid.

m.p. 66-67 °C (Et$_2$O:hexane)

$\nu_{\text{max}} / \text{cm}^{-1}$: (solid) 2865 (m), 1596 (m), 1339 (s), 1155 (s).

$\delta_H$ (400 MHz, CDCl$_3$) 7.73 (2H, d, J = 8.5 Hz, ArCH), 7.31 (2H, d, J = 8.5 Hz, ArCH), 5.83 – 5.79 (1H, m, C5-H), 5.76 – 5.71 (1H, m, C6-H), 4.55 (1H, dd, J = 8.0, 2.0 Hz, C4-H), 3.36 (1H, ddd, J = 9.5, 7.0, 4.5 Hz, C1-H), 3.10 – 3.02 (1H, m, C1-H'), 2.61 (1H, ddd, J = 8.0, 8.0, 8.0, 7.5, 2.0 Hz, C3-H), 2.53 – 2.44 (1H, m, C7-H), 2.42 (3H, s, Ts CH$_3$), 2.10 (1H, ddd, J = 17.0, 2.0, 2.0 Hz, 1H, C7-H'), 1.88 – 1.79 (1H, m, C2-H), 1.51 (1H, ddd, J = 12.5, 7.5, 7.5, 7.0 Hz, C2-H').

$\delta_C$ (101 MHz, CDCl$_3$) 143.4 (ArC), 134.9 (ArC), 132.0 (C6), 131.4 (C5), 129.7 (ArCH), 127.7 (ArCH), 70.2 (C4), 48.4 (C1), 40.0 (C3), 38.1 (C7), 32.5 (C2), 21.6 (Ts CH$_3$).

HRMS: (ESI$^+$) Calculated for C$_{14}$H$_{17}$NNaO$_2$: 286.0872. Found [M+Na]$^+$: 286.0873.

**1-Tosyl-2-vinylpyrrolidine (8d)**

![Ts

$\delta_H$ (400 MHz, CDCl$_3$) 7.71 (2H, d, J = 8.0 Hz), 7.30 (2H, d, J = 8.0 Hz), 5.80 (1H, ddd, J = 17.0, 10.0, 6.0 Hz), 5.27 (1H, ddd, J = 17.0, 1.5, 1.5 Hz), 5.11 (1H, ddd, J = 10.0, 1.5, 1.5 Hz), 4.13 (1H, ddd, J = 6.0, 6.0, 6.0, 1.5, 1.5 Hz), 3.44 (1H, ddd, J = 10.0, 7.0, 4.5 Hz), 3.23 (1H, ddd, J = 10.0, 7.5, 7.5 Hz), 2.42 (3H, s), 1.87 – 1.73 (1H, m), 1.73 – 1.55 (3H, m).

A yield of 80% was achieved when this reaction was performed on a 1.40 mmol scale.

m.p. 69-70 °C (Et$_2$O:hexane) [Lit., 70 °C (no recrystallization solvent quoted)]$^{30}$

$\nu_{\text{max}} / \text{cm}^{-1}$: (solid) 2986 (m), 2957 (m), 1595 (m), 1460 (m), 1335 (s), 1154 (s), 1088 (s), 1000 (s).
$\delta C$ (101 MHz, CDCl$_3$) 143.4, 138.8, 135.3, 129.7, 127.6, 115.4, 62.0, 48.9, 32.4, 23.9, 21.6.

$m/z$ (ESI$^+$) 274 ([M+Na]$^+$, 100 %), 252 ([M+H]$^+$, 20 %).

The spectroscopic properties were consistent with the data available in the literature.$^{30}$

**(E)-2-Styryl-1-tosylpyrrolidine (8e)**

![Chemical structure](image)

**General procedure G:** Conditions: 2.5 mol % Pd$_2$(dba)$_3$; 12.5 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 25 mol % Et$_3$N; $n$-BuCN (0.1 M); 110 °C; 15 hours. Substrate 7e (75.5 mg, 0.140 mmol) was employed. FCC (9:1 hexane:EtOAc) afforded 8e (35.4 mg, 77 %) as a pale yellow oil.

$\delta H$ (400 MHz, CDCl$_3$) 7.72 (2H, d, $J = 8.0$ Hz), 7.33 – 7.18 (7H, m), 6.54 (1H, d, $J = 16.0$ Hz), 6.04 (1H, dd, $J = 16.0$, 6.5 Hz), 4.34 (1H, ddd, $J = 7.0$, 6.5, 4.5 Hz), 3.48 (1H, ddd, $J = 10.0$, 7.0, 4.5 Hz), 3.34 (1H, ddd, $J = 10.0$, 7.0, 7.0 Hz), 2.39 (3H, s), 1.94 – 1.79 (2H, m), 1.77 – 1.65 (2H, m).

$\delta C$ (101 MHz, CDCl$_3$) 143.3, 136.7, 135.7, 130.7, 130.1, 129.7, 128.6, 127.7, 127.6, 126.6, 61.8, 48.8, 32.9, 24.1, 21.6.

The spectroscopic properties were consistent with the data available in the literature.$^{31}$

**2-Methyl-1-mesyl-2-vinylpyrrolidine (8f)**

![Chemical structure](image)
General procedure G: Conditions: 3.75 mol % Pd\(_2\)(dba); 18.75 mol % P(3,5-(CF\(_3\))\(_2\)C\(_6\)H\(_3\)); 25 mol % Et\(_3\)N; 6:1 n-BuCN:DMF (0.1 M); 110 °C. Substrate 7f (56.7 mg, 0.140 mmol) was employed. FCC (10:1 PhMe:EtOAc) afforded 8f (21.3 mg, 80 %) as a pale yellow oil.

\(\nu_{\text{max}} / \text{cm}^{-1}\): (film) 2976 (m), 2928 (m), 1330 (s), 1148 (s).

\(\delta\)H (400 MHz, CDCl\(_3\)) 5.98 (1H, dd, \(J = 17.5, 10.5 \text{ Hz, } \text{C}5-\text{H}\)), 5.24 (1H, dd, \(J = 17.5, 0.5 \text{ Hz, } \text{C}6-\text{H}'\)), 5.15 (1H, dd, \(J = 10.5, 0.5 \text{ Hz, } \text{C}6-\text{H}\)), 3.53 – 3.44 (2H, m, \text{C}1-\text{H}'), 2.86 (3H, s, Ms CH\(_3\)), 2.04 – 1.97 (1H, m, C2-\text{H} and C3-\text{H}'), 1.57 (3H, s, C7-\text{H}).

\(\delta\)C (101 MHz, CDCl\(_3\)) 142.1 (C5), 114.0 (C6), 67.0 (C4), 49.5 (C1), 41.7 (C3), 39.7 (Ms CH\(_3\)), 25.1 (C7), 22.4 (C2).

HRMS: (ESI') Calculated for C\(_8\)H\(_{15}\)NNaO\(_2\)S: 212.0716. Found [M+Na]: 212.0714.

1-Mesyl-1-azaspiro[4.5]dec-6-ene (8g)

![1-Mesyl-1-azaspiro[4.5]dec-6-ene (8g)](image)

General procedure G: Conditions: 3.75 mol % Pd\(_2\)(dba); 18.75 mol % P(3,5-(CF\(_3\))\(_2\)C\(_6\)H\(_3\)); 25 mol % Et\(_3\)N; 6:1 n-BuCN:DMF (0.1 M); 110 °C; 16 hours. Substrate 7g (59.8 mg, 0.140 mmol) was employed. FCC (29:1 PhMe:acetone) afforded 8g (12.8 mg, 42 %) as a yellow crystalline solid.

\(\nu_{\text{max}} / \text{cm}^{-1}\): (solid) 3023 (m), 2929 (m), 1447 (m), 1317 (s), 1143 (s).

\(\delta\)H (400 MHz, CDCl\(_3\)) 5.82 (1H, ddd, \(J = 10.0, 5.5, 2.5 \text{ Hz, } \text{C}6-\text{H}\)), 5.62 – 5.57 (1H, m, C5-\text{H}), 3.57 (1H, ddd, \(J = 10.5, 6.0, 3.5 \text{ Hz, } \text{C}1-\text{H}'\)), 3.42 – 3.34 (1H, m, C1-\text{H}''), 2.89 (3H, s, Ms CH\(_3\)), 2.35 (1H, ddd, \(J = 13.0, 13.0, 3.5 \text{ Hz, } \text{C}9-\text{H}\)), 2.09 (1H, dddd, \(J = 16.5, 11.0, 5.5, 2.5 \text{ Hz, } \text{C}7-\text{H}\)), 2.02 – 1.78 (6H, m, C2-\text{H} and C3-\text{H}'), 1.77 – 1.68 (1H, m, C9-\text{H}''), 1.58 – 1.47 (1H, m, C8-\text{H}').

\(\delta\)C (101 MHz, CDCl\(_3\)) 131.5 (C5), 129.2 (C6), 66.6 (C4), 49.2 (C1), 41.1 (C3), 40.0 (Ms CH\(_3\)), 34.4 (C9), 24.3 (C7), 22.6 (C2), 21.6 (C8).

HRMS: (ESI') Calculated for C\(_{10}\)H\(_{17}\)NNaO\(_2\)S: 238.0872. Found [M+Na]: 238.0878.

2-Benzyl-1-mesyl-2-vinylpyrrolidine (8h)
 General procedure G: Conditions: 5.0 mol % Pd$_2$(dba)$_3$; 25 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 25 mol % Et$_3$N; n-BuCN (0.1 M); 95 °C; 16 hours. Substrate 7h (66.8 mg, 0.140 mmol) was employed. FCC (gradient elution 5:1 – 3:1 hexane:EtOAc) afforded 8h (19.9 mg, 54 %) as a pale yellow oil.

ν$_{\text{max}}$/ cm$^{-1}$: (film) 3027 (m), 2978 (m), 1602 (m), 1496 (m), 1318 (s), 1144 (s).

δH (500 MHz, CDCl$_3$) 7.32 – 7.27 (4H, m, ArCH), 7.25 – 7.21 (1H, m, ArCH), 6.24 (1H, dd, J = 17.5, 11.0 Hz, C$_5$-H), 5.27 (1H, dd, J = 11.0, 0.5 Hz, C$_6$-H), 5.26 (1H, dd, J = 17.5, 0.5 Hz, C$_6$-$H'$), 3.40 (1H, d, J = 13.5 Hz, C$_7$-H), 3.35 – 3.26 (2H, m, C$_1$-H$_2$), 3.06 (1H, d, J = 13.5 Hz, C$_3$-$H'$), 1.71 – 1.62 (1H, m, C$_2$-H), 1.34 (1H, dddd, J = 14.0, 12.5, 7.0, 7.0 Hz, C$_2$-$H'$).

δC (126 MHz, CDCl$_3$) 140.3 (C$_5$), 137.3 (ArC), 131.1 (ArCH), 128.2 (ArCH), 126.7 (ArCH), 115.5 (C$_6$), 70.1 (C$_4$), 49.9 (C$_1$), 44.7 (C$_7$), 39.4 (Ms CH$_3$), 36.4 (C$_3$), 22.4 (C$_2$).

HRMS: (ESI$^+$) Calculated for C$_{14}$H$_{19}$NNaO$_2$: 288.1029. Found [M+Na]$^+$: 288.1017.

3-Phenyl-1-tosyl-2-vinylpyrrolidine (8i)

 General procedure G: Conditions: 2.5 mol % Pd$_2$(dba)$_3$; 12.5 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 25 mol % Et$_3$N; n-BuCN (0.1 M); 110 °C; 16 hours. Substrate 7i (75.5 mg, 0.140 mmol) was employed. FCC (gradient elution, 9:1 – 4:1 hexane:EtOAc) afforded 8i (37.2 mg, 81 %, 2:1 mixture of trans and cis diastereomers) as a colorless oil.

ν$_{\text{max}}$/ cm$^{-1}$: (film) 3029 (m), 2979 (m), 1598 (m), 1345 (s), 1159 (s).

Spectroscopic data for the major trans diastereomer:
δ\text{H} (400 MHz, CDCl\textsubscript{3}) 7.74 (2H, d, J = 8.0 Hz), 7.38 – 7.16 (5H, m), 6.95 – 6.89 (2H, m), 5.86 (1H, ddd, J = 17.0, 10.5, 7.0 Hz), 5.08 (1H, d, J = 10.5 Hz), 5.06 (1H, d, J = 17.0 Hz), 3.97 (1H, ddd, J = 17.0, 10.5, 7.0 Hz), 3.74 – 3.63 (1H, m), 3.53 (1H, ddd, J = 11.0, 9.0, 6.5 Hz), 3.07 (1H, ddd, J = 9.5, 7.0, 7.0 Hz), 2.47 (3H, s), 2.18 – 2.01 (1H, m), 1.76 – 1.59 (1H, m).

δ\text{C} (101 MHz, CDCl\textsubscript{3}) 143.4, 140.1, 137.6, 135.4, 129.6, 128.5, 127.6, 127.4, 127.0, 116.2, 69.5, 52.0, 48.6, 32.3, 21.6.

Characteristic signals for the minor cis diastereomer:

δ\text{H} (400 MHz, CDCl\textsubscript{3}) 7.80 (2H, d, J = 8.0 Hz), 5.38 – 5.24 (2H, m), 4.52 (1H, dd, J = 8.0, 4.5 Hz), 3.35 (1H, ddd, J = 10.0, 10.0, 7.0 Hz), 2.31 – 2.20 (1H, m).

The spectroscopic properties were consistent with the data available in the literature.\textsuperscript{32}

cis-2-Cyclopropyl-1-tosyl-5-vinylpyrrolidine (8j)

\[
\text{\includegraphics[width=0.2\textwidth]{cis-2-cyclopropyl-1-tosyl-5-vinylpyrrolidine.png}}
\]

**General procedure G:** Conditions: 5.0 mol % Pd\text{2}(dba)\textsubscript{3}; 25 mol % P(3,5-(CF\textsubscript{3})\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{3}; 25 mol % Et\textsubscript{3}N; PhMe (0.1 M); 140 °C; 15 hours. Substrate 7j (76.3 mg, 0.152 mmol, added as a solution in PhMe) was employed. FCC (9:1 hexane:EtOAc) afforded 8j (33.2 mg, 75 %, 13:1 mixture of cis and trans diastereomers) as a colorless crystalline solid.

ν\text{max} / cm\textsuperscript{-1}: (film) 3007 (m), 2967 (m), 1598 (m), 1494 (m), 1344 (s), 1158 (s).

Spectroscopic data for the major cis diastereomer:

δ\text{H} (400 MHz, CDCl\textsubscript{3}) 7.71 (2H, d, J = 8.0 Hz, Ar\text{CH}), 7.27 (2H, d, J = 8.0 Hz, Ar\text{CH}), 5.86 (1H, ddd, J = 17.0, 10.5, 6.0 Hz, C\textsubscript{7}-H), 5.29 (1H, ddd, J = 17.0, 1.5, 1.5 Hz, C\textsubscript{8}-H\textsuperscript{1}), 5.10 (1H, ddd, J = 10.5, 1.5, 1.5 Hz, C\textsubscript{8}-H\textsuperscript{2}), 4.17 – 4.10 (1H, m, C\textsubscript{6}-H), 3.26 (1H, ddd, J = 8.0, 8.0, 4.0 Hz, C\textsubscript{3}-H), 2.41 (3H, s, Ts CH\textsubscript{3}), 1.78 – 1.71 (2H, m, C\textsubscript{5}-H\textsubscript{2}), 1.70 – 1.61 (1H, m, C\textsubscript{4}-H), 1.57 – 1.46 (1H, m, C\textsubscript{4}-H\textsuperscript{1}), 0.96 (1H, dddt, J = 8.0, 8.0, 8.0, 5.0 Hz, C\textsubscript{2}-H), 0.62 – 0.49 (2H, m, C\textsubscript{1}-H\textsubscript{2}), 0.48 – 0.39 (1H, m, C\textsubscript{1}-H\textsuperscript{1}), 0.25 – 0.17 (1H, m, C\textsubscript{1}-H\textsuperscript{1}).

δ\text{C} (101 MHz, CDCl\textsubscript{3}) 143.1 (Ar\textsuperscript{C}), 139.5 (C\textsubscript{7}), 136.2 (Ar\textsuperscript{C}), 129.4 (Ar\textsuperscript{CH}), 127.6 (Ar\textsuperscript{CH}), 115.4 (C\textsubscript{8}), 65.9 (C\textsubscript{3}), 63.3 (C\textsubscript{6}), 31.2 (C\textsubscript{5}), 30.3 (C\textsubscript{4}), 21.5 (Ts CH\textsubscript{3}), 16.9 (C\textsubscript{2}), 4.7 (C\textsubscript{1}), 2.8 (C\textsubscript{1}-H\textsuperscript{1}).
Characteristic signals for the minor trans diastereomer:

δ_H (400 MHz, CDCl₃) 5.77 (1H, ddd, J = 17.0, 10.0, 7.5 Hz), 5.20 (1H, ddd, J = 17.0, 1.0, 1.0 Hz), 5.06 (1H, ddd, J = 10.0, 1.0, 1.0 Hz), 4.42 (1H, dd, J = 7.5; 7.5 Hz).


cis-1-MesyI-2-phenyl-5-vinylpyrrolidine (8k)

General procedure G: Conditions: 5.0 mol % Pd₂dba; 25 mol % P(3,5-(CF₃)₂C₆H₃); 25 mol % Et₃N; 6:1 n-BuCN:DMF (0.1 M); 120 °C; 19 hours. Substrate 7k (64.9 mg, 0.140 mmol) was employed. FCC (gradient elution, 10:1 – 5:1 – 2:1 hexane:EtOAc) afforded 8k (20.4 mg, 58 %) as a pale yellow oil.

ν_max / cm⁻¹: (film) 3029 (m), 2934 (m), 1451 (m), 1328 (s), 1145 (s).

δ_H (400 MHz, CDCl₃) 7.41 – 7.32 (4H, m, ArCH), 7.31 – 7.26 (1H, m, ArCH), 6.02 (1H, ddd, J = 17.0, 10.0, 7.0 Hz, C5-H), 5.40 (1H, ddd, J = 17.0, 1.0, 1.0 Hz, C6-H'), 5.27 (1H, ddd, J = 10.0, 1.0, 1.0 Hz, C6-H), 5.00 (1H, dd, J = 7.0, 7.0 Hz, C1-H), 4.59 (1H, br ddd, J = 7.5, 7.0, 7.0 Hz, C4-H), 2.66 (3H, s, Ms CH₃), 2.40 – 2.30 (1H, m, C2-H), 2.17 (1H, ddd, J = 12.0, 7.5, 7.5, 6.0 Hz, C3-H), 2.01 (1H, dddd, J = 12.5, 7.0, 6.0, 6.0 Hz, C2-H'), 1.95 – 1.86 (1H, m, C3-H').

δ_C (101 MHz, CDCl₃) 142.2 (ArC), 138.7 (C5), 128.7 (ArCH), 127.7 (ArCH), 126.9 (ArCH), 117.2 (C6), 64.7 (C1), 63.3 (C4), 41.3 (Ms CH₃), 35.1 (C2), 31.5 (C3).

**cis-2-Butyl-1-mesyl-5-vinylpyrrolidine (8l)**

![Structure of cis-2-Butyl-1-mesyl-5-vinylpyrrolidine (8l)](image)

**General procedure G:** Conditions: 5.0 mol % Pd₂dba₃; 25 mol % P(3,5-(CF₃)₂C₆H₃); 25 mol % Et₃N; PhMe (0.1 M); 140 °C; 20 hours. Substrate 7l (62.1 mg, 0.140 mmol) was employed. FCC (5:1 hexane:EtOAc) afforded 8l (19.9 mg, 61 %, 14:1 ratio of cis and trans diastereomers) as a pale yellow oil.

νₘᵢₓ / cm⁻¹: (film) 2932 (m), 1331 (s), 1148 (s).

*Spectroscopic data for the major cis diastereomer:*

δ_H (400 MHz, CDCl₃) 5.79 (1H, ddd, J = 17.0, 10.0, 6.5 Hz, C⁹-H), 5.30 (1H, ddd, J = 17.0, 1.5, 1.5 Hz, C¹⁰-H), 5.14 (1H, dd, J = 10.0, 1.5, 1.5 Hz, C¹⁰-H), 4.29 – 4.23 (1H, m, C⁸-H), 3.81 – 3.74 (1H, m, C⁵-H), 2.84 (3H, s, Ms CH₃), 2.10 – 1.93 (2H, m, C⁶-H and C⁷-H'), 1.92 – 1.76 (2H, m, C⁴-H and C⁷-H'), 1.72 – 1.62 (1H, m, C⁶-H'), 1.47 – 1.22 (5H, m, C²-H₂, C³-H₂ and C⁴-H'), 0.90 (3H, t, J = 7.0 Hz, C₁-H₃).

δ_C (101 MHz, CDCl₃) 139.4 (C⁹), 116.1 (C¹⁰), 62.9 (C⁸), 61.8 (C⁵), 38.8 (Ms CH₃), 36.5 (C⁴), 31.7 (C⁷), 30.2 (C⁶), 28.7 (C₂ or C₃), 22.7 (C₂ or C₃), 14.2 (C₁).

¹_H NMR spectrum for the minor trans diastereomer:

δ_H (500 MHz, CDCl₃) 5.79 (1H, ddd, J = 17.0, 10.0, 8.5 Hz), 5.53 (1H, ddd, J = 17.0, 1.0, 1.0 Hz), 5.18 (1H, ddd, J = 10.0, 1.0, 1.0 Hz), 4.30 (1H, dd, J = 8.5 Hz), 3.74 – 3.68 (1H, m), 2.86 (3H, s), 2.26 – 2.18 (1H, m), 2.11 – 1.95 (2H, m), 1.80 (1H, ddt, J = 13.0, 6.5, 1.5 Hz), 1.70 (1H, ddt, J = 12.5, 6.5, 1.5 Hz), 1.48 – 1.39 (1H, m), 1.38 – 1.19 (5H, m), 0.90 (3H, t, J = 7.0 Hz).


**(2S*,5R*)-5-Cyclopropyl-2-methyl-1-tosyl-2-vinylpyrrolidine (8m)**
General procedure G: Conditions: 5.0 mol % Pd$_2$(dba)$_3$; 25 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 25 mol % Et$_3$N; PhMe (0.1 M); 140 °C; 14 hours. Substrate 7m (79.6 mg, 0.154 mmol, added as a solution in PhMe) was employed. FCC (two times: first eluent 19:1 hexane:EtOAc, second eluent 99:1 PhMe:EtOAc) afforded 8m (30.1 mg, 64 %, 20:1 mixture of diastereomers) as a pale yellow oil.

$\nu_{\text{max}}$ / cm$^{-1}$: (film) 3084 (m), 2972 (m), 1599 (m), 1496 (m), 1327 (s), 1151 (s).

Spectroscopic data for the major diastereomer:

$\delta_H$ (400 MHz, CDCl$_3$) 7.77 (2H, d, $J = 8.0$ Hz, ArCH), 7.22 (2H, d, $J = 8.0$ Hz, ArCH), 6.10 (1H, dd, $J = 17.5$, 10.5 Hz, C7-H), 5.23 (1H, dd, $J = 17.5$, 1.0 Hz, C8-H'), 5.08 (1H, dd, $J = 10.5$, 1.0 Hz, C8-H), 3.33 (1H, ddd, $J = 8.5$, 7.5, 1.5 Hz, C3-H), 2.15 (1H, ddd, $J = 12.5$, 12.0, 6.5 Hz, C5-H), 2.01 (1H, dddd, $J = 12.5$, 12.5, 8.5, 6.5 Hz, C4-H), 1.77 – 1.66 (2H, m, C4-H' and C5-H'), 1.55 (3H, s, C9-H$_3$), 0.90 (1H, dddd, $J = 8.5$, 8.5, 5.0, 5.0 Hz, C2-H), 0.53 – 0.46 (1H, m, C1-H), 0.44 – 0.32 (2H, m, C1'-H' and C1''-H').

$\delta_C$ (101 MHz, CDCl$_3$) 145.1 (C7), 142.4 (ArC), 140.7 (ArC), 129.1 (ArCH), 127.7 (ArCH), 115.9 (C8), 69.0 (C6), 66.7 (C3), 40.1 (C5), 29.6 (C4), 24.4 (C9), 21.6 (Ts CH$_3$), 17.1 (C2), 7.2 (C1), 2.8 (C1').

Characteristic signals for the minor diastereomer:

$\delta_H$ (500 MHz, CDCl$_3$) 5.91 (1H, dd, $J = 17.5$, 11.0 Hz), 5.17 (1H, dd, $J = 17.5$, 1.0 Hz), 5.02 (1H, dd, $J = 11.0$, 1.0 Hz).

HRMS: (ESI$^+$) Calculated for C$_{17}$H$_{23}$NNaO$_2$: 328.1342. Found [M+Na]$^+$: 328.1353.

Methyl (E)-2-(1-tosylpyrrolidin-2-ylidene)acetate (8n)
General procedure G: Conditions: 2.5 mol % Pd$_2$(dba)$_3$; 12.5 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 25 mol % Et$_3$N; 6:1 $n$-BuCN:DMF (0.1 M); 110 °C; 15 hours. Substrate 7n (71.0 mg, 0.140 mmol) was employed. FCC (gradient elution, 3:1 – 2:1 hexane:EtOAc) afforded 8n (32.4 mg, 78 %) as a pale yellow oil.

$\nu_{\text{max}}/\text{cm}^{-1}$: (film) 2950 (m), 1707 (s), 1620 (s), 1346 (s), 1129 (s).

$\delta$H (400 MHz, CDCl$_3$) 7.75 (2H, d, $J = 8.0$ Hz, ArC$_6$H$_3$), 7.32 (2H, d, $J = 8.0$ Hz, ArCH), 6.03 (1H, t, $J = 2.0$ Hz, C$_5$H), 3.76 (2H, t, $J = 7.0$ Hz, C$_1$H$_2$), 3.64 (3H, s, OCH$_3$), 3.03 (2H, td, $J = 7.5$, 2.0 Hz, C$_3$H$_2$), 2.42 (3H, s, Ts C$_6$H$_3$), 1.88 (2H, tt, $J = 7.5$, 7.0 Hz, C$_2$H$_2$).

δC (101 MHz, CDCl$_3$) 168.3 (C$_6$), 156.9 (C$_4$), 145.0 (ArC), 134.3 (ArC), 130.0 (ArCH), 127.4 (ArCH), 94.9 (C$_5$), 51.0 (OCH$_3$), 32.4 (C$_3$), 21.7 (Ts CH$_3$), 21.3 (C$_2$).

HRMS: (ESI$^+$) Calculated for C$_{14}$H$_{17}$NNaO$_4$: 318.0770. Found [M+Na$^+$]: 318.0780.

8-Mesy1-8-azabicyclo[3.2.1]oct-2-ene (8o)

General procedure G: Conditions: 5.0 mol % Pd$_2$(dba)$_3$; 25 mol % P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_3$; 25 mol % Et$_3$N; 6:1 $n$-BuCN:DMF (0.1 M); 110 °C; 16 hours. Substrate 7o (55.9 mg, 0.140 mmol) was employed. FCC (gradient elution, 5:1 – 4:1 – 3:1 hexane:EtOAc) afforded 8o (15.6 mg, 60 %) as a colorless crystalline solid.

$\nu_{\text{max}}/\text{cm}^{-1}$: (solid) 3046 (m), 2958 (m), 2926 (m), 1458 (m), 1321 (s), 1137 (s).

$\delta$H (400 MHz, CDCl$_3$) 5.99 (1H, dddd, $J = 9.5$, 5.5, 2.0, 2.0 Hz, C$_2$H), 5.62 – 5.56 (1H, m, C$_3$H), 4.33 – 4.25 (2H, m, C$_1$H and C$_5$H), 2.93 (3H, s, Ms C$_6$H$_3$), 2.77 – 2.67 (1H, m, C$_4$H), 2.31 – 2.20 (1H, m, C$_6$H), 2.13 – 1.90 (3H, m, C$_4$H$^+$ and C$_7$H$_2$), 1.77 – 1.67 (1H, m, C$_6$H$^+$).

δC (101 MHz, CDCl$_3$) 131.5 (C$_2$), 124.1 (C$_3$), 55.6 (C$_1$ or C$_5$), 55.5 (C$_1$ or C$_5$), 40.9 (Ms C$_6$H$_3$), 36.1 (C$_7$), 35.6 (C$_4$), 30.8 (C$_6$).
HRMS: (ESI⁺) Calculated for C₈H₁₄NO₂S: 188.0740. Found [M+H]⁺: 188.0744.

**ORTEP view of 8o**

6-Mesyl-6-azabicyclo[3.2.1]oct-3-ene (8p)

**General procedure G**: Conditions: 5.0 mol % Pd₂(dbach₃); 25 mol % P(3,5-(CF₃)₂C₆H₃)₃; 25 mol % Et₃N; 1:1 n-BuCN:THF (0.1 M); 110 °C, 17 hours. Substrate 7p (55.9 mg, 0.140 mmol) was employed, FCC (9:1 PhMe:EtOAc) afforded 8p (19.9 mg, 76 %) as a colorless crystalline solid.

m.p. 61-62 °C (Et₂O:hexane, cubes)

νₘₚ / cm⁻¹: (solid) 3034 (m), 2967 (m), 1312 (s), 1133 (s).

δH (400 MHz, CDCl₃) 6.06 (1H, dddd, J = 10.5, 5.5, 2.0, 1.0 Hz, C₅-H), 5.73 – 5.68 (1H, m, C₆-H), 4.17 (1H, ddd, J = 5.5, 5.0, 1.0 Hz, C₄-H), 3.64 – 3.59 (1H, m, C₁-H), 3.09 (1H, d, J = 10.0 Hz, C₁-H’), 2.81 (3H, s, Ms C₆H₃), 2.72 – 2.67 (1H, m, C₂-H), 2.55 – 2.47 (1H, m, C₇-H), 2.16 – 2.09 (1H, m, C₇-H’), 1.95 (1H, ddd, J = 11.0, 5.0, 5.0 Hz, C₃-H), 1.83 (1H, ddd, J = 11.0, 1.0, 1.0 Hz, C₃-H’).
δC (101 MHz, CDCl₃) 129.8 (C5), 128.5 (C6), 54.1 (C1), 54.0 (C4), 37.7 (Ms CH₃), 35.6 (C7), 34.7 (C3), 33.4 (C2).


ORTEP view of 8p

2-Mesy1-1-vinyl-1,2,3,4-tetrahydroisoquinoline (8q)

General procedure G: Conditions: 5.0 mol % Pd₂dba₃; 25 mol % P(3,5-(CF₃)₂C₆H₃)₃; 25 mol % Et₃N; 6:1 n-BuCN:DMF (0.1 M); 110 °C; 19 hours. Substrate 7q (62.9 mg, 0.140 mmol) was employed. FCC (gradient elution, 9:1 – 7:1 – 4:1 – 2:1 hexane:EtOAc) afforded 8q (14.1 mg, 42 %) as a pale yellow oil.

νmax / cm⁻¹: (film) 3022 (m), 2931 (m), 1492 (m), 1452 (m), 1327 (s), 1151 (s).

δH (500 MHz, CDCl₃) 7.22 – 7.18 (2H, m, ArCH), 7.17 – 7.13 (1H, m, ArCH), 7.12 – 7.08 (1H, m, ArCH), 6.02 (1H, ddd, J = 17.0, 10.0, 6.5 Hz, C4-H), 5.40 (1H, br d, J = 6.5 Hz, C3-H), 5.28 (1H, ddd, J = 10.0, 1.5, 1.5 Hz, C5-H), 5.21 (1H, ddd, J = 17.0, 1.5, 1.5 Hz, C5-H'), 3.91 (1H, ddd, J =
13.5, 6.5, 2.5 Hz, C1-H), 3.37 (1H, ddd, J = 13.5, 11.5, 4.5 Hz, C1-H’), 3.07 (1H, ddd, J = 16.5, 11.5, 6.5 Hz, C2-H), 2.83 (3H, s, Ms CH3), 2.79 (1H, ddd, J = 16.5, 4.5, 2.5 Hz, C2-H’).

δc (126 MHz, CDCl3) 136.8 (C4), 133.7 (ArC), 133.3 (ArC), 129.2 (ArCH), 128.0 (ArCH), 127.3 (ArCH), 126.4 (ArCH), 118.1 (C5), 58.2 (C3), 39.7 (Ms CH3), 39.2 (C1), 28.2 (C2).


7-Methylene-1-mesyl-1-azaspiro[4.4]nonane (8r)

General procedure G: Conditions: 3.75 mol % Pd2(dba)3; 18.75 mol % P(3,5-(CF3)2C6H3)3; 25 mol % Et3N; 6:1 n-BuCN:DMF (0.1 M); 110 °C; 16 hours. Substrate 7r (59.8 mg, 0.140 mmol) was employed. FCC (gradient elution 4:1 – 2:1 hexane:EtOAc) afforded 8r (25.9 mg, 86 %) as a colorless crystalline solid.

m.p. 64-66 °C (Et2O:hexane, cubes)

νmax / cm⁻¹: (solid) 3069 (m), 2930 (m), 1655 (m), 1311 (s), 1143 (s).

δh (400 MHz, CDCl3) 4.89 – 4.86 (1H, m, C8-H), 4.83 – 4.80 (1H, m, C8-H’), 3.51 – 3.37 (2H, m, C1-H2), 3.09 (1H, ddd, J = 15.5, 3.0, 3.0, 3.0 Hz, C9-H), 2.86 (3H, s, Ms CH3), 2.59 – 2.42 (2H, m, C5-H and C6-H), 2.27 – 2.16 (2H, m, C6-H’ and C9-H’), 1.90 – 1.74 (4H, m, C2-H2 and C3-H2), 1.65 (1H, ddd, J = 10.0, 6.0, 2.0 Hz, C5-H’).

δc (101 MHz, CDCl3) 147.8 (C7), 107.4 (C8), 72.0 (C4), 50.0 (C1), 44.4 (C9), 40.1 (C3), 39.3 (Ms CH3), 36.3 (C5), 29.8 (C6), 22.6 (C2).


Mitsunobu inversion study:

(R)-N-(1-phenylethyl)-N-(pentafluorobenzyloxy)-4-toluenesulfonylamine
**General procedure A**: (S)-1-Phenylethanol (58.0 mg, 0.475 mmol, 99 % e.e.) and 4a were employed, FCC (eluents 250:1 hexane:EtOAc followed by PhMe) afforded the title compound (178 mg, 74 %, 96 % e.e.) as a crystalline colorless solid.

\[ \alpha \]_D^24 = -9.1 (c 4.25, CHCl₃)

**SFC conditions**: column: CHIRALPACK IC, elute: 10 % MeOH/CO₂, detector: 250 nm, flow rate: 3 mL/min, temperature: 40 °C, retention times: (R) t₁ = 3.6 min, (S) t₂ = 3.9 min.

ν_max / cm⁻¹: (solid) 2988 (m), 1791 (s), 1658 (m), 1597 (m), 1509 (s), 1167 (s).

Two species were observed in the \(^1\)H and \(^1^3\)C NMR spectra in an approximately 2:1 ratio. These are presumably a pair of diastereomers generated as a result of the nitrogen center not being sp² hybridized. The signals were also very broad, likely due to slow inversion of the nitrogen centre.

δ H (500 MHz, CDCl₃) 7.79 (2H, br s, ArCH), 7.52 – 7.12 (7H, m, ArCH), 5.41 – 4.73 (1H, m, C1-H), 2.46 (3H, s, Ts CH₃), 1.65 (3H, br s, C2-H₃).

δ C (126 MHz, CDCl₃) 155.9 (Fbz C=O), 145.6 (ArC), 138.5 (ArC), 132.5 (ArC), 129.7 (ArCH), 129.3 (ArCH), 128.4 (ArCH), 128.2 (ArCH), 127.9 (ArCH), 63.1 (C1), 60.4 (C1’), 21.7 (Ts CH₃), 21.0 (C2), 15.4 (C2’).

The aromatic signals corresponding to the pentafluorobenzoyl group could not be resolved due to their weak intensity.

δ F (377 MHz, CDCl₃) -135.9 (2F, br s), -146.0 – -146.5 (1F, m), -159.2 (2F, br s).

References

$^{1}H$ and $^{13}C$ NMR spectra of novel compounds

TsNHO$^5$Bz

[Graph of NMR spectra]

single pulse decoupled gated NOE
MsNHOH